

Iron In Natural Garnets: Heat And Irradiation Induced Changes

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ABSTRACT: The optical absorption spectra of some natural single crystal garnets from Izom, Nigeria have been measured in the visible and UV (14,000 – 35,000 cm^{-1}) region of light spectrum. Room temperature spectra of the garnets show absorption peaks due to ferric and ferrous ions in octahedral and dodecahedral coordination respectively. Mn^{2+} absorption bands are also present in the spectra. Upon heating in air to 650 $^{\circ}\text{C}$, the Fe^{3+} absorption bands at 20,200; 21,700; 23,300; 27,250 and 29,200 cm^{-1} become enhanced in intensities while the Mn^{2+} bands at 20,800 and 21,050 cm^{-1} disappeared. The Fe^{3+} bands in the spectra become slightly depressed after heating in charcoal and are not too noticeable because of the intense nature of the Fe^{3+} bands in the spectra. X-irradiation produced enhancements of Fe^{2+} bands at 16,200 17,600 cm^{-1} and Mn^{4+} band at 27,200 cm^{-1} respectively. Because of its broadness, the intense broad band at 29,200 cm^{-1} is hereby interpreted to be due to Fe^{2+} Fe^{3+} charge transfer. However, no changes in the optical spectra was produced after treatment with UV light. [New York Science Journal. 2009;2(4):64-73]. (ISSN: 1554-0200).

Keywords: Spectra, natural garnet, absorption band, heating, x- irradiation, UV light.

INTRODUCTION

Garnets constitute a silicate mineral species with variable crystallo-chemical properties and mode of occurrence. This diversity is brought about in part by the ability of the garnet structure to accommodate cations with a wide range of sizes and valence states. Garnets also possess a wide variety of colours mainly resulting from incorporation of very different types and amounts of transition elements into X (dodecahedral), Y (octahedral), and Z (tetrahedral) coordination sites. The colours exhibited vary from white to shades of red, brown, yellow, green and black, depending on the transition ion impurities and their concentration.

The interrelationship between chemistry and crystal structure of garnet has been the subject of a considerable amount of research in the past three decades within three fields of scientific interest. In the earth science, the garnets are studied because of their importance as rock forming minerals in the earth's crust and upper mantle (Carbno and Canil, 2002). They occur as stable phases in a wide range of pressures, temperatures and chemical environments. Although they are most commonly associated with contact (Gaspar et al, 2008) and regional metamorphic rocks, they are also found in igneous rocks ranging from granites to peridotites (Batumike et al, 2001) as well as in felsic volcanics and pegmatites. Secondly, in solid state physics, synthetic non-silicate garnets are investigated because of their ferrimagnetic and laser properties. Thirdly, garnets are useful as gemstones in jewellery in which colour is one of the important properties because it contributes greatly to the value of gems. Garnets are one of the best gemstones, therefore, studies on their colour phenomena become both of economic and scientific interest.

Optical absorption spectroscopy is of potential use to characterize site occupancy in crystals both qualitatively (by observation and assignment of spectral bands to specific cation in specific sites, Burns, 1970a) and quantitatively (by comparison of spectral intensities, Burns, 1970b). However, as the distribution of ions among the different cation sites is likely to vary depending on the genesis of the particular garnet, the optical spectrum is thus expected to be a useful tool for the determination of site distribution of the ions. Therefore, attempts have been made to characterize site occupancies in the

garnets. The complexity of the garnet spectra, however, makes some assignments and interpretations uncertain.

The optical absorption spectra of natural almandine single crystal garnets from Izom, Central Nigeria, have been measured in the visible and near UV regions of light spectrum (14,000-35,000 cm^{-1}) and optical absorption bands of Fe have been identified and characterized. Earlier absorption band studies by Manning (1967, 1967a, 1970a, 1970b and 1972), Slack and Chrenko (1971), White and Moore (1972), Runciman and Sengupta (1974), Newman et al, (1978), Kholer and Amthauer (1970) and Chaunyi (1981) on garnets have not only identified absorption bands due to Fe^{3+} , Fe^{2+} , Cr^{3+} , Mn^{2+} and other impurity cations but also assigned them to cation coordination sites (X, Y and Z). However, the optical absorption spectra of the silicate garnets in the 14,000 – 35,000 cm^{-1} region are perhaps the most complicated observed for any mineral. As many as 15 to 20 distinct bands have so far been reported in this relatively narrow spectral range.

The present study is an attempt to understand the response of Fe in the garnet crystal structure to heating, irradiation and UV light treatments. Changes observed are expected to contribute to knowledge of the crystal chemistry and colour of garnets. An attempt is made to explain the observed changes in the Fe and Mn optical absorption spectra and also to assign the band at 29,200 cm^{-1} , which has hitherto not been assigned (cf. Manning, 1967).

MATERIALS AND METHODS

Garnet Samples

The specimens used consisted of five wine red almandine garnet crystals. The crystals were collected from Izom, near Abuja in central Nigeria. The samples were selected for crystallinity, size and phase purity. Generally, the crystals measured about 2cm by 1cm and are big enough for optical absorption studies. Perfectly oriented wavers were cut from each of the crystals and polished on both sides to thickness of approximately 1.7mm. Preliminary transmitted light spectroscopy studies indicated that the crystals show colour zoning. Care was taken to ensure that areas of uniform colour and enough width were selected for the optical absorption spectral study.

Chemical Analysis

The garnets were chemically analysed by electron microprobe for seven major and trace elements. In these analyses, all of the Fe has been assumed to occur as Fe^{2+} . However, Utsunomiya et al, (2005) have shown that although Fe in unirradiated natural garnets consist dominantly of Fe^{2+} ions, some Fe^{3+} ions are also present. Indeed, the spectra of the unirradiated natural samples in this study contain Fe^{3+} absorption bands.

Optical Absorption Spectra

Optical absorption spectra were recorded in the range 14,000-35,000 cm^{-1} by means of a Cary Model 14R spectrophotometer. All spectra were run at room temperature. The diameter of the spectrophotometer measuring circular slit was 2mm. The optical absorption spectral measurement method of Cohen et al (1985) was employed. Garnet belongs to the cubic system, and has identical spectra in all orientations to the polarized light. Therefore, only the normal light spectrum has been measured. All absorbance values reported here and shown in the figures are accurate to within approximately $\pm 2\%$ verified using standard absorption screens.

Heat Treatment Experiments

Heating in oxidizing (air) and reducing (charcoal) conditions was done in order to observe if any changes would occur in the colour or intensities of absorption bands of Fe and Mn in the spectra. The samples were heated in air to see whether or not oxidation of Fe^{2+} and Mn^{2+} would take place. This was done by placing the sample on a very clean block of high-purity fused silica and heating in an electric furnace for 3hours at 650°C.

The sample was similarly heated in charcoal, which was used as a reducing medium for 3 hours at 650°C. Care was taken to ensure that the sample was completely covered by the charcoal powder. Optical absorbance measurements were taken as in the oxidizing condition.

X-irradiation

Ion irradiation effects in garnets have recently become a subject of topical research interest (Eby et al, 2001; Calligaro et al, 2002; Utsunomiya et al, 2002 (a); 2002 (b); 2005). The samples were subjected to X-irradiation for 24 hours from a 50KV source run at 35ma. The sample was wrapped in aluminum foil before it was put in the cell for irradiation in order to minimize the possible bleaching action of ambient light.

UV Light Treatment

The optically good crystals were illuminated with UV light produced by a high pressure Xenon-Mercury lamp to observe if any colour change would occur. Illumination time was four hours after which the samples were cooled to room temperature and the absorption spectra taken.

RESULTS

The results of electron microprobe analyses for the major and trace elements are shown in Table 1. The analyses show that the garnets are enriched in Mn. Figure 1 and Table 2 show the optical absorption bands of the room temperature normal spectrum of unirradiated almandine garnet. The bands at 27.260 and 29.200cm⁻¹ displayed broad intensities (Figs. 1, 2 and 3). The spectra obtained after heating in air indicated that the Fe³⁺ bands at 20,000; 21,700; 23,300 and 27,260cm⁻¹ became enhanced in intensities.

Table 1. Electron microprobe analysis of almandine garnets (All results in wt. percent)

	AD1	AD2	AD3	AD4	AD5
SiO ₂	37.12	37.39	37.23	37.20	37.18
Al ₂ O ₃	20.00	19.78	20.15	20.26	20.05
TiO ₂	0.05	0.03	0.03	0.02	0.01
FeO	34.01	34.32	34.27	34.15	34.18
MgO	3.01	22.96	2.98	3.02	3.01
MnO	2.63	2.71	2.69	2.62	2.73
CaO	3.18	2.78	2.65	2.75	2.83
	100.00	99.97	100.00	100.02	99.99

Table 2. Survey of reported bands (cm⁻¹) of Fe in natural almandine garnets at room temperature

Electron Volts (eV)	Manning (1967)	Slack and Chrenko (1971)	White (1972)	Moore and (1972)	This work (650°C)	This work	Assignment
1.80	14.500	14.500	14.500	14.700	14.680	(Fe ²⁺)viii	
2.02+	16,300	16,300	16.300	16.200	16.150+	(Fe ²⁺)viii	
2.19+	17.500	17.500	17.470	17.600	16.600+	(Fe ²⁺)viii	
2.38	19.200	19.200	19.200	19.200	19.200	(Fe ²⁺)viii	
2.46	19.800	19.800	19.850	20,000	20.000	(Fe ²⁺)viii	
2.58					20.800	20.800	D Mn ²⁺
2.61					21.250	21.050	D Mn ²⁺
2.70+	21.800	21.700	21.650	21.800	21.700+	(Fe ²⁺)vi	
2.89+	23.500	23.900	23.350	23.300	23.300+	(Fe ²⁺)vi	
3.10	25.100		25.025				(Fe ²⁺)viii

3.39+	→	27.300	27.650	27.200	27.200	27.200+	(Fe ²⁺)vi	→	Mn ⁴⁺	
362+		29.000		→		29.200	29.200+	Fe ²⁺	→	Fe ³⁺

D = disappeared

+ = enhanced upon heating and X – irradiation

The yet unassigned band at 29.200 cm⁻¹ also became enhanced in intensity while the Mn²⁺ bands at 20.800 and 21.050cm⁻¹ disappeared (Figs. 2a, 2b and 2c). The Fe³⁺ became slightly depressed after heating in charcoal. X-irradiation produced enhancements of Fe²⁺ bands at 16.200 and 17.600 cm⁻¹ and Mn⁴⁺ band at 27,200 cm⁻¹ (Fig 3) respectively. However, no changes in the optical spectra were produced after treatment with UV light.

DISCUSSION

The results of the microprobe analyses of representative samples of the garnets used for optical absorption spectra studies are shown in Table 1. Of the transition ions present in the samples, iron is found to be most abundant. Generally, iron containing garnets exhibit some of the complicated visible spectra yet observed in transition ion-containing minerals. These are due to the spin-forbidden transitions of Fe³⁺ and Fe²⁺. Garnet spectra also often contain optical bands of other cations especially Mn²⁺, Mn⁴⁺ etc.

The structure of garnets has been described by many authors, notable among who are Gibbs and Smith (1965) and Novak and Gibbs (1971). Based on the structure, various workers, like Maning (1967), Slack and Chrenko (1971), Moore and White (1972), Runciman and Sengupta (1974), Huggins et al (1977) and Chuanyi (1981) have attempted to assign Fe³⁺ and Fe²⁺ to coordination sites in garnets (Table 2). These assignments remain uncertain because of the complexity of the garnet spectra. Apart from the high variety of impurity cations (transition ions) that can enter the structure, garnets display efficient packing of oxygen in their structure (Meagher, 1982). The efficiency in packing is brought about by the lack of tetrahedral polymerization and the large number of shared polyhedral edges. This latter factor inhibits easy diffusion of cations in the structure even at high temperatures.

All the optical bands obtained for natural garnets in the present study very closely correspond to those from previous studies. The spectra for heated and irradiated garnets are however not, until now, known to have been reported; nor has the observed band at 29,200 cm⁻¹ been previously explained or assigned (cf. Manning, 1967). The bands at 21,700 and 27,260 cm⁻¹ have been previously assigned to Fe³⁺ in the octahedral site. These assignments and interpretations, however, need to be re-considered and particularly in the light of the obtained chemical composition of the garnets (Table 1). The present analyses of these samples now compel us to take another careful look at these earlier assignments and interpretations. It is particularly important to also consider the contribution of optical bands of Mn to the general spectra. Heating and X-irradiation treatments reported here have assisted in explaining, at least, part of these phenomena. The quantity of Mn in the studied samples (Table 1) indicates that the Mn²⁺ and Mn⁴⁺ ions play some role in the development of the garnet spectra after heating and X-irradiation. Bands due to Mn²⁺ have been found to occur at 20,050cm⁻¹ while those due to Mn⁴⁺ either as spin allowed or spin-forbidden occur at 16,200; 16,400; 16,800; 22,700; 23,200; 26,600 and 27,200 cm⁻¹. This is bound to affect the spectral bands of both ions in a mineral rich in both elements. It is hereby proposed that the observed changes in spectra after heating and X-irradiation involve Fe²⁺, Mn²⁺ and Mn⁴⁺ and not only Fe³⁺ and Fe²⁺ as previously interpreted (Manning, 1972).

Heating in air produced enhancement in intensities of the bands at 20,000; 21,700; 23,300; 27,260 and 29,300 cm⁻¹ as a result of oxidation of Fe²⁺ to Fe³⁺. The Mn²⁺ bands at 20,800 and 21,050 cm⁻¹ disappeared in the process also because of oxidation of Mn²⁺ to Mn⁴⁺. The oxidation of both Fe²⁺ and Mn²⁺ ions is an easy process because they

occur in the dodecahedral sites and are not tightly bonded like those occurring in the octahedral sites. On heating in charcoal, the Fe³⁺ bands became only slightly depressed indicating slight reduction of Fe³⁺ to Fe²⁺. This is because the structure of garnets and the octahedral coordination of Fe³⁺ make its dislodgment from the site difficult. Because the Fe³⁺ bands are intense and broad, these depressions in intensities are not too noticeable. The process of X-irradiation involving Fe³⁺ and Mn²⁺ can be considered to proceed as follows: $Mn^{2+} + 2Fe^{3+} \rightarrow Mn^{4+} + 2Fe^{2+}$.

This process explains the enhancement of intensities of the Fe²⁺ bands at 16,200 and 17,600cm⁻¹ and Mn⁴⁺ band at 27,200cm⁻¹. This observation is in agreement with the findings of Utsunomiya et al (2005). The enhancements at 16,200 and 17,600cm⁻¹ are due to the produced Fe²⁺ and also that at 27,200 cm⁻¹ is due in part to contribution from the produced Mn⁴⁺. The band at 29,200 cm⁻¹ became enhanced in intensity on X-irradiation. This is due to reaction of the produced Fe²⁺ with nearest neighbour Fe³⁺ giving Fe²⁺ Fe³⁺ intervalence charge transfer band (Manning, 1973). The broadness and intensity of this band make this assignment more likely than any other. Also, samples elsewhere that have not shown optical bands due to Fe³⁺ do not have this band in their spectra.

Exposure of the samples to UV light was to see if any bleaching of the colour would occur. There was no change in the colour or intensity of the spectra of the garnets. It shows that the colour of garnet is not affected by exposure to UV light or X-irradiation. This property recommends the crystals as good gemstones.

CONCLUSION

The following conclusions can be drawn from this study. The optical absorption bands in almandine garnet crystals are affected by heating and X-irradiation. Bands of Fe³⁺ and Mn⁴⁺ are enhanced on heating in air and X-irradiation as a result of oxidation of Fe³⁺ and Mn²⁺ to Mn⁴⁺. Overlap and interaction of Mn⁴⁺ and Fe²⁺ bands at 16,200cm⁻¹ and Mn⁴⁺ band at 27,200cm⁻¹ respectively are the causes of the enhancements of intensities of these bands. These observed bands therefore, are results of combination of bands of both ions and not just bands due to a single ion (Fe³⁺ or Fe²⁺) as previously interpreted.

Also, the band at 29,200 cm⁻¹ is Fe²⁺ → Fe³⁺ intervalence charge transfer band. It will occur only in garnets that contain appreciable amounts of Fe³⁺ content. The crystals are not bleached by heating, X-irradiation or UV light. This indicates that the colour producing ions in garnets are tightly held in their crystal structure and hence cannot change their valences easily. Therefore, in terms of suitability their colour stability recommends them as valuable gemstones. However, they will still be required to satisfy other necessary requirements like crystallinity, size, phase purity and durability.

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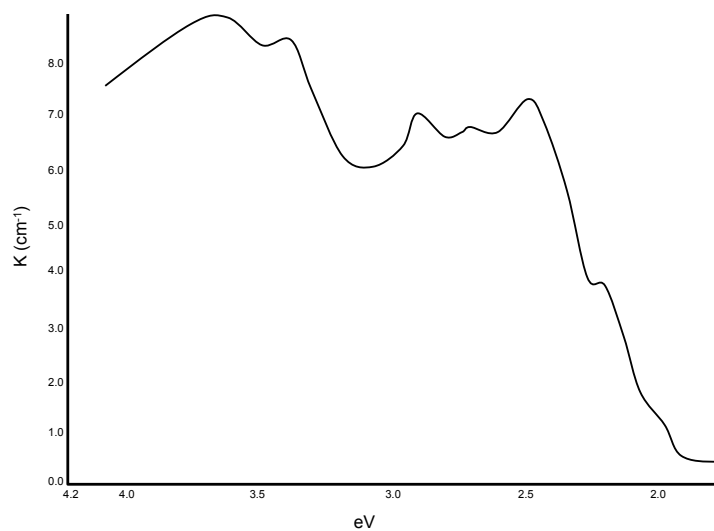


Fig 1: Absorption spectrum of natural almandine garnet single crystal using normal light

Fig 2a

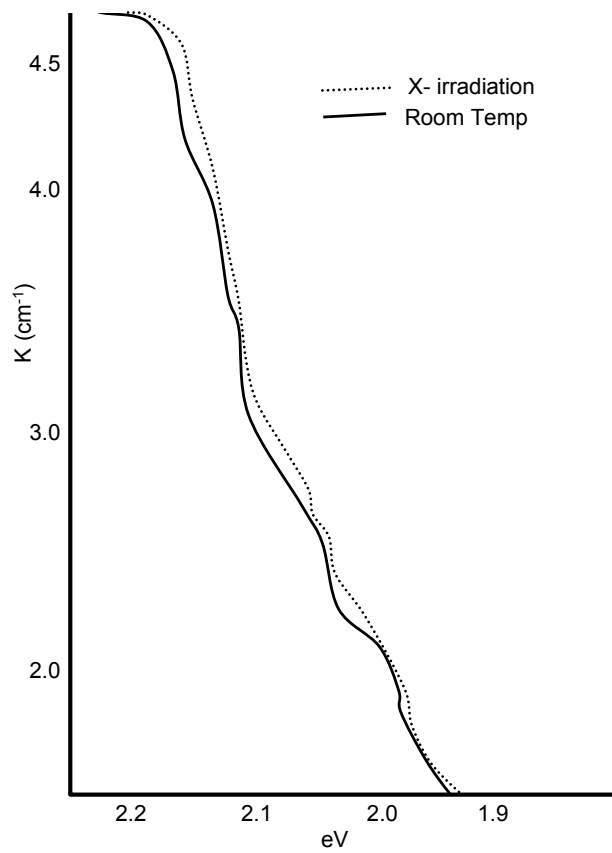


Fig 2b

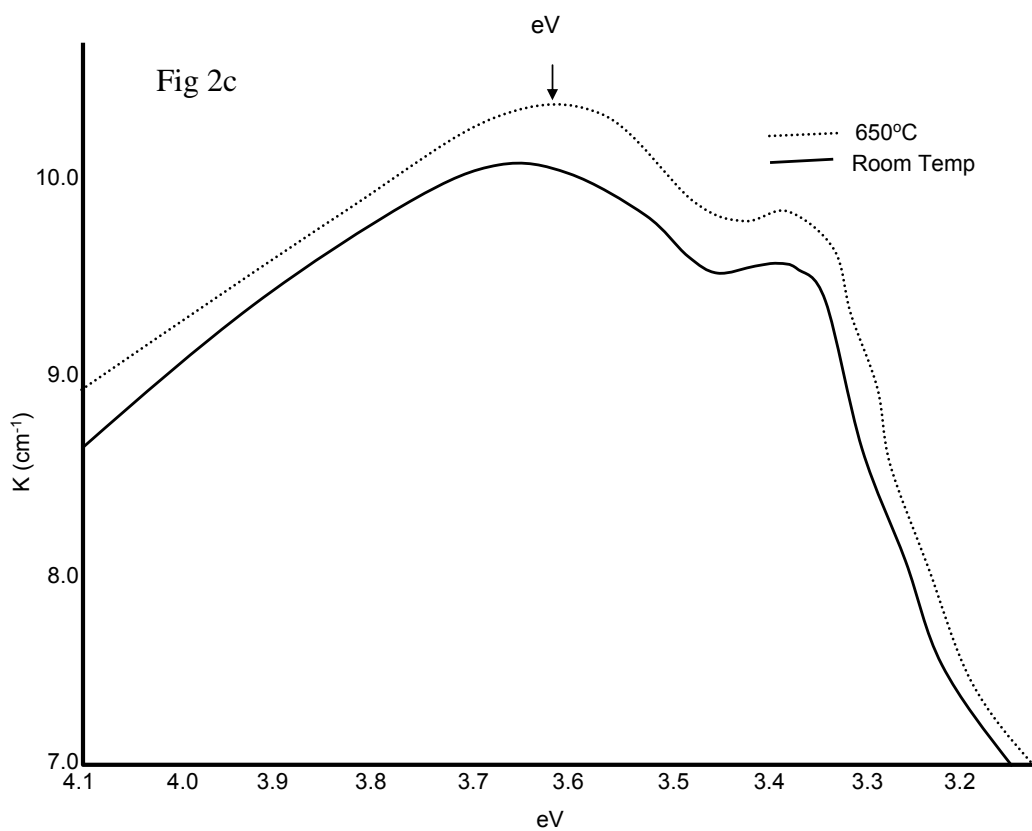
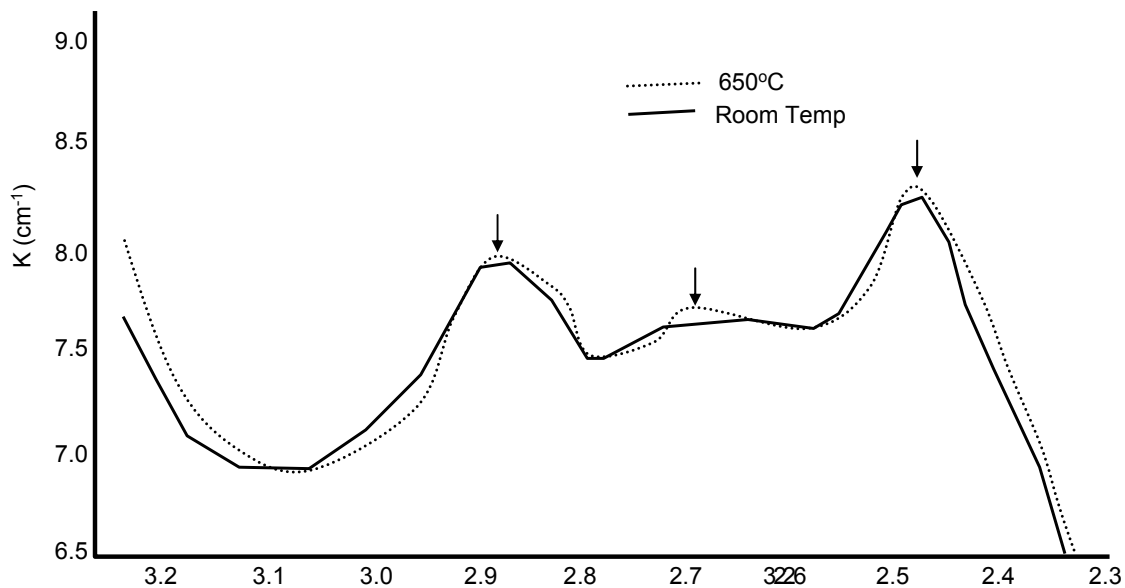
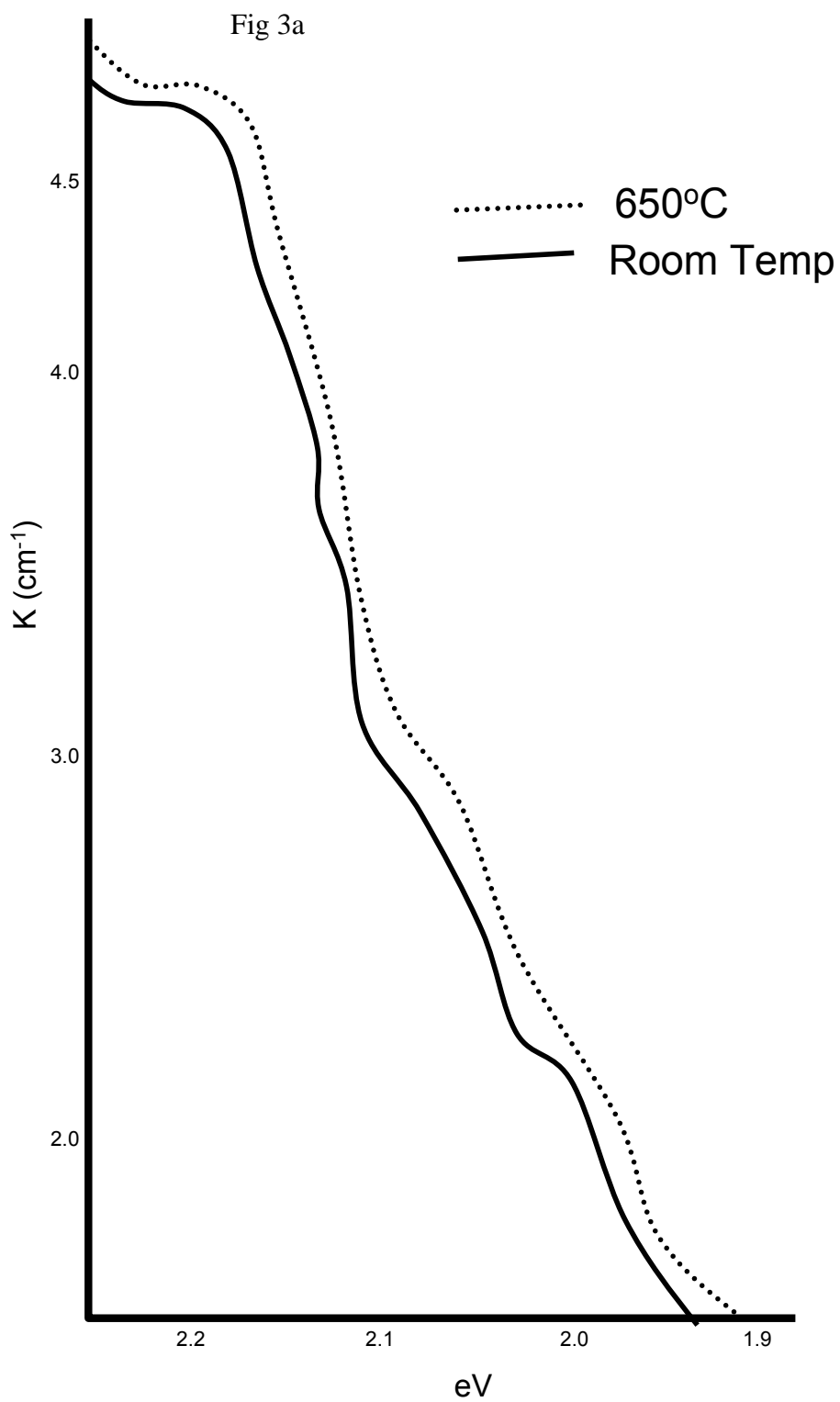


Fig 2a, 2b,2c: Absorption spectra showing changes after heating at 650°C



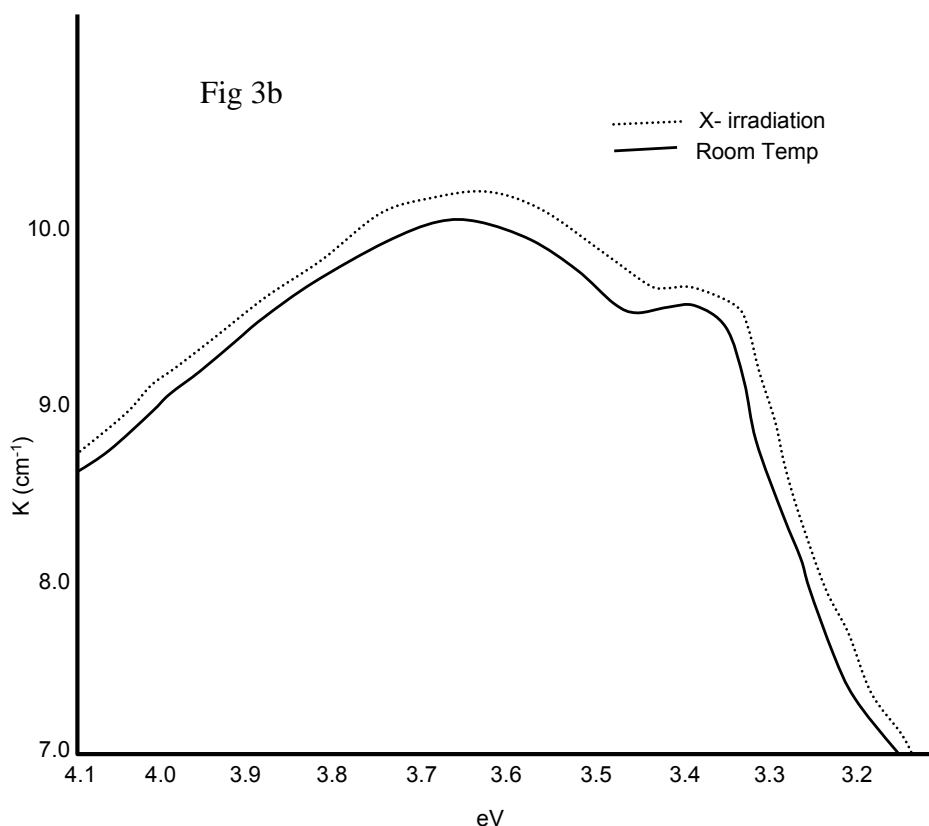


Fig 3a,3b: Absorption spectra showing changes after X- irradiation

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