

Optical Absorption Spectra Of Chromium In Cassiterite Single Crystals

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Abstract: Recently, much interest is being shown in the physical properties of cassiterite because of its insulating and semiconducting properties. Of particular interest is the doped cassiterite crystals which have found good uses in varistor ceramic and colour pigmentation. The addition of chromium and some transition elements into the cassiterite lattice has resulted in the modification of the properties of pure cassiterite. The absorption spectra of cassiterite (SnO₂) single crystals doped with chromium were studied by absorption spectrophotometry in order to investigate colour pigmentation in cassiterite. These crystals are coloured red and it was found that absorption is greater in doped crystals than in undoped ones. Spectral bands due to Cr³⁺ and Cr²⁺ were detected using normal light. The bands compare well with those in other chromium containing materials. Heating the crystals to 700°C under reducing conditions caused large decreases in the spectral intensity of the Cr³⁺ band at 2.3eV. Gamma irradiation of these crystals also produced similar effects. The results obtained here and published data elsewhere suggest that the reduction in the Cr³⁺ band was caused by the ionizing effects on the Cr³⁺ ion to produce Cr²⁺ and Cr⁴⁺ ions. There was no change in the colouration of the crystal even after heating under reducing condition or gamma-irradiation. This is interpreted to mean that a lot of the Cr³⁺ ions have entered the substitutional Sn⁴⁺ site in the crystal lattice where they are tightly bonded and cannot easily change their valence states.”[The Journal of American Science 2009; 5(4);141-145]. (ISSN 1545 - 1003)”

Keywords: cassiterite crystal, gamma-irradiation, absorption spectra, chromium-doped cassiterite, crystal lattice

1.0 Introduction

In the past few decades, many research workers have investigated the colour center phenomena in solids (Arkhangelskii et al, 1967,1968). Initially, studies on colour centers were mainly confined to alkali halides. But, after the advent of the different techniques of growing synthetic crystals, these studies were extended to other solids as well. Recently, much interest is being shown in the physical properties of cassiterite because of its insulating and semiconducting properties. Of particular interest is the pigmentation. The addition of chromium and some transition elements into the doped cassiterite crystals which have found good uses in varistor ceramic and colour cassiterite lattice has resulted in the modification of the properties of pure cassiterite (Moreira et al, 2006). The optical absorption of pure crystals has been studied by Reddaway and Wright (1965) and Wright (1968). They observed a band in the region of 3.5 eV which was ascribed to oxygen deficiency or some unknown impurities. However, Cohen et al (1985) were able to clearly identify the band to be due to Sn²⁺. Hou et al (1967) and Lopez-Navarete et al (2003), have done some work on Cr-doped cassiterite single crystals. It is felt that the level of research work on these materials is rather low and therefore a systematic and correlated study on them

is necessary. Also, the effect of chromium impurity on colouration of cassiterite is rather faintly understood. The purpose of the present paper is to report on the changes in the optical absorption spectra of chromium doped SnO₂ single crystals heated under reducing conditions and irradiated with gamma-rays at room temperature.

2.0 Materials and Methods

Two red cassiterite crystals were studied. The paler sample NMNH 136748 was obtained from the Mineralogy Branch of the National Museum of Natural History, Washington, D.C. There is no chemical analysis of this sample. The more intense coloured sample C110k was obtained from J. A. Marley and its preparation was described in Marley and MacAvoy (1961). The chemical analysis of the undoped sample was given in Cohen et al (1985) and this sample has been doped with 250ppm chromium by Hou et al (1967). The Cr³⁺ and Cr²⁺ soda-silicate glasses studied were those prepared by Smith and Cohen (1963).

Methods of sample preparation for optical studies have been described in Cohen et al (1985). However, sample NMNH 136748 was too small to cut in the basal section and only its axial spectrum was measured. Sample C110K was cut into two, the axial and basal sections, and their spectra were

measured. The axial sections of the crystals are less than 1mm and do not cover the 2mm hole in the sample holder. Therefore, matching small holes that are 0.4mm in diameter were specially made for use in the optical absorption measurements. The smallness of the holes made it impossible to measure the polarized spectra of these crystals.

Heat treatment and gamma-irradiation experiments were done as earlier described by Cohen et al (1985). Optical measurements were made on a Cary Model 14 Spectrophotometer at room temperature. The Gaussian resolution of the bands was done using Dupont Model 301 Curve resolver.

3.0 Results

The optical absorption spectra at room temperature of chromium doped cassiterite crystals are presented in Figure 1. The crystals have optical absorption bands due to Cr^{3+} at 1.80, 2.28 and 2.88 eV. These bands increase in intensity with increase in chromium content. This is illustrated by comparing the absorption heights of the two samples in Figure 1 with the intensely coloured C110k sample having higher absorption coefficients than that of the paler NMNH 136748. The polarized spectra of the as grown cassiterite crystals were taken at room temperature and are shown in Figure 2.

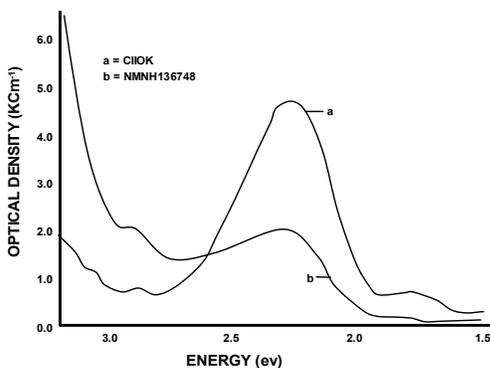


Fig. 1: Absorption spectra of chromium doped cassiterite single crystals using normal light

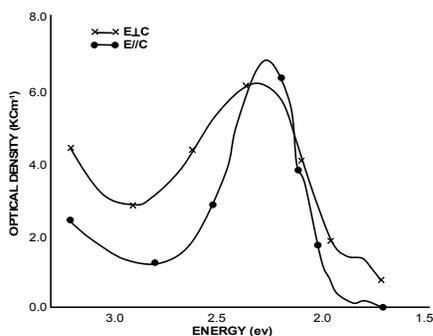


Fig. 2: Polarized spectra of chromium doped cassiterite single crystals

Observed bands for the electric vector (E) of light parallel to c-axis (E//c) are found at 1.78 and 2.25 eV. The band at 2.88eV could not be distinctively resolved. For the electric vector (E) of light perpendicular to c-axis (E1c), the bands are at 1.83 and 2.3eV. Table 1 gives the peak positions of the Cr^{3+} and Cr^{2+} bands compared with those in other chromium containing materials. In Table 2, the details of the polarized spectra of the crystals are given. The absorption spectra of chromium doped cassiterite irradiated with gamma rays at room temperature showing the bands due to Cr^{2+} and Cr^{3+} are presented in Figure 3. There was no change in colour but there was a decrease in the absorption coefficient of the broad band in the 2.3eV region. This is an indication that the Cr^{3+} ions causing the band have decreased as a result of gamma-irradiation. New bands at 2.43 and 2.63eV developed.

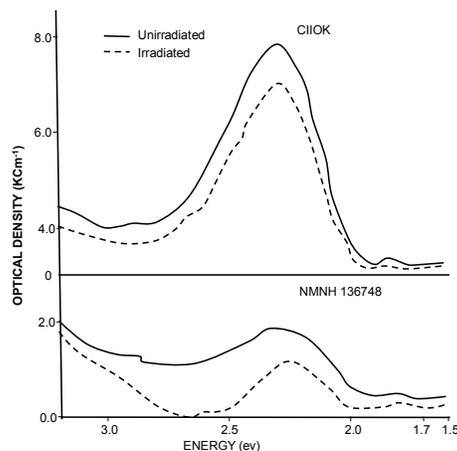


Fig. 3: Absorption spectra of Chromium doped cassiterite showing changes after gamma irradiation

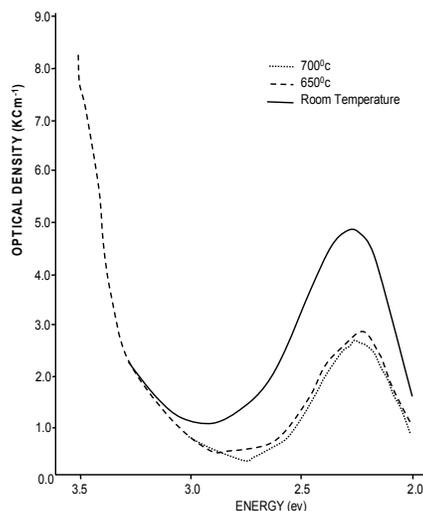


Fig. 4: Changes in spectrum of C110K on heating from room temperature to 700°C

Table 1: Peak positions (in eV) of Cr²⁺ and Cr³⁺ absorption bands in soda silicate glass, cassiterite and other materials.

Specimen	Cr ³⁺	Cr ²⁺	Cr ³⁺	Cr ³⁺ Cr ²⁺	Cr ²⁺	Cr ³⁺	Author
Glass: Cr ²⁺		1.90		2.41	2.65		1
Glass: Cr ³⁺	1.80		1.96				1
Ruby	1.78			2.29			2
Cassiterite				2.30			3
NMNH							
136748	1.80			2.28		2.88	4
CIIOK	1.80			2.29		2.89	4
(reduced)				2.43	2.63		4
1.	Smith and Cohen (1963)						
2.	Marcfarlane (1963)						
3.	Hou et al (1967)						
4.	Present work						

Table 2: Peak positions (in eV) of spectra of as grown and reduced crystals of chromium doped cassiterite.

E//C	As Grown		Reduced		Author
	E1c	E//c	E1c	E1c	
	2.26	2.44	2.65		1
1.78	1.83	2.44	2.49		2
2.25	2.30	2.60	2.65		2
1.	Hou et al (1967)				
2.	Present work				

Heating of the samples in a reducing environment produced new bands similar to those developed during gamma-irradiation. There was a marked decrease in the absorption band in the 2.3eV region at 700°C. Thereafter, no further significant reduction in the band occurred as shown in Figure 4. There was also no change in the colour of the samples. Although Hou et al (1967) reported complete disappearance of the main band at 2.3eV, this has not been recorded in this work. The difference in our results may be due to the types of reducing agents used. While they used a mixture of nitrogen and hydrogen, the reducing agent used in this work was silicon carbide (SiC). It is reasonable to suppose that because at high temperature (>500°C), ionic diffusion into crystal lattices becomes easy, hydrogen will diffuse into the structure and combine with oxygen to produce OH group. This is why they got the OH stretching vibration absorption band in their spectra. Losos and Beran (2004) also reported the presence of OH defect in cassiterite. The causes of some of these bands have not yet been ascertained.

4.0 Discussion

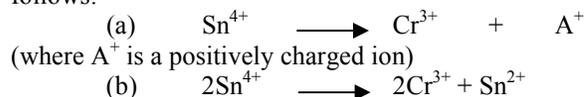
The phenomena of colouration in ionic crystals such as alkali halides have been well understood and the colouration mechanism has been explained in terms of the trapping of electrons and holes liberated during irradiation process at proper vacancy sites (anion and cation vacancies). These vacancies are either inherently present in the crystal lattice or have been induced by irradiation process. In SnO₂, the lattice energy is considerably higher than in the monovalent alkali halides and as such ionizing radiation would not be very effective in generating new defects as in alkali halides.

Cassiterite has the tetragonal rutile structure in which each tin atom is at the center of six oxygen placed approximately at the corners of a regular octahedron. However, this octahedral site is tetragonally distorted. Three bands corresponding to the transitions:

${}^4A_{2g} \longrightarrow {}^2E_g$ (1.80eV), ${}^4A_{2g} \longrightarrow {}^4T_{2g}$ (2.28eV), ${}^4A_{2g} \longrightarrow {}^4T_{1g}$ (2.88eV) are predicted for Cr³⁺ and similar transition ions like Fe³⁺ and Ti⁴⁺ in this environment (Marcfarlane, 1963; Wood et al, 1963; Desausoy et al, 1988; Lopez-Navarete et al, 2003). Chromium-doped cassiterite features these bands which compare well with values obtained for Cr³⁺ in glass and other materials.

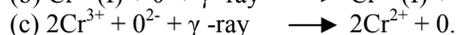
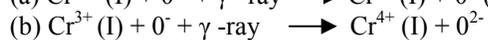
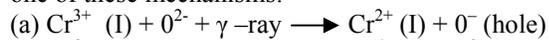
In the cassiterite lattice, there are vacant cation (Sn⁴⁺) and anion (O²⁻) sites as well as interstitial sites. Cr³⁺ (0.70A⁰) ions can substitute for Sn⁴⁺ (0.77A⁰) as given by Shannon (1976). Cr³⁺ ions can also occupy the interstitial octahedral sites which are larger than the substitutional octahedral sites (Hurlen, 1959). Wittke (1965) worked on the diffusion of transition metal ions into the rutile structure and found that at least seventy per cent of the chromium ions are preferentially found in substitutional sites. The EPR work of Hou et al (1967) and Ruck et al (1989) also confirm this for Cr³⁺ in cassiterite. Hence in cassiterite, over seventy per cent of the Cr³⁺ ions enter the substitutional octahedral sites while the remaining thirty percent enters the octahedral interstitial site.

During the incorporation of Cr³⁺ ions into the crystal lattice, it will enter the vacant cation site. The amount entering the Sn⁴⁺ site will depend on the amount of pre-existing cation vacancies in the crystal. Cr³⁺ is one charge less than Sn⁴⁺ and there will be need for a charge compensator for charge balance near Cr³⁺ (Brehat et al, 1990). However, a doubly charged cation can compensate for two Cr³⁺ ions. These two situations can be considered as follows:



In (b), Sn^{2+} acts as a compensator between the two Cr^{3+} ions and that is probably why it is difficult for it to change its valence state during heating and gamma irradiation (Cohen et al, 1985).

Upon exposure to gamma rays, the absorption coefficient of Cr^{3+} decreases. This is evidence that some Cr^{3+} ions have changed valence states. Also, oxygen ion would be singly or doubly ionized. The electrons released from the oxygen ions will be trapped at impurity sites or anion vacancies. The change in valence states of Cr^{3+} can occur via one of these mechanisms:



In (a), the oxygen ion loses an electron which is captured by Cr^{3+} to become Cr^{2+} , while it becomes a "hole". A Cr^{3+} ion can capture a hole to become a Cr^{4+} ion as shown in (b). When the two electrons on the oxygen ion are ejected, then the situation depicted in (c) arises whereby neutral oxygen atoms are produced. In this work, no band due to Cr^{4+} has been identified. This is probably because the Cr^{4+} bands are masked by the more intense Cr^{3+} bands. Thus, in the chromium doped cassiterite, there can coexist simultaneously Cr^{2+} , Cr^{3+} and Cr^{4+} (Lopez-Navarete et al, 2003). There is also the Sn^{2+} in octahedral interstitial sites. Gamma irradiation gave rise to new bands at 2.43 and 2.63eV. Maruyama and Matsuda (1964) studied chromium doped ruby single crystals and ascribed the band at 2.43 eV to Cr^{2+} . Govinda (1976) also studied chromium-doped ruby single crystals and ascribed the band at 2.65eV to Cr^{2+} . Thus, the bands at 2.43 and 2.63eV are accordingly ascribed to Cr^{2+} produced by conversion of interstitial Cr^{3+} .

There was no evidence for the formation of additional colour centers by gamma-irradiation as there was no change in the colour of the samples. Additional colour center formation is likely inhibited as a result of high concentration of chromium doping. A possible reason for this is that at high concentrations, the inherent defect concentration becomes considerably reduced. Another possible reason is that the reduction in the concentration of cation vacancies may act as a hinderance to the easy dislodgement of electrons from O^{2-} ions during gamma-irradiation. The interpretation given by Hou et al (1967) that Cr^{3+} ions exist in different environments in the crystal lattice, i.e. substitutional and interstitial sites is correct. However, they erred by suggesting that Cr^{3+} ions were leaping in and out of the substitutional sites during their reduction experiments. This is unlikely because a lot of bond energy would be required to free the strongly bonded substitutional Cr^{3+} ion. Rather, the thirty per cent

Cr^{3+} ions they considered to be leaping out of the substitutional sites are indeed the Cr^{3+} ions that changed valence states during reduction or gamma-irradiation. These are the interstitial Cr^{3+} ions.

5.0 Conclusion

The colour of chromium doped cassiterite is due to the amount of Cr^{3+} ions present in the substitutional cation sites in the crystal lattice. Gamma-irradiation and heating under reducing conditions led to production of Cr^{2+} and Cr^{4+} ions. Because there is no colour change during production of Cr^{2+} and Cr^{4+} , these ions are not the colour centers causing the observed colour. The Cr^{3+} ions that changed valence states are considered to be interstitially located. Irradiation effects are considered to relate only to the preexisting imperfections in the crystal lattice (cation and anion vacancies) and to the changes in the valence states of Cr^{3+} ions.

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