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Causes of the purple and pink colours of manganoan sugilites from the Wessels mine, South Africa

THE occurrence of manganoan sugilite at the Wessels Mine near Kuruman, South Africa, has been described by Wilson and Dunn (1978), Dunn *et al.* (1980), de Villiers (1983), Dixon (1985), and more recently by von Bezing *et al.* (1991). A detailed chemical analysis of this material (Taggart *et al.*, 1994) is available elsewhere in this issue. Shigley *et al.* (1987) discussed the gemological properties of this material, and reported that although most manganoan sugilite from the Wessels mine is purple, it also occurs very rarely with a reddish purple colour (commonly described as pink). While illustrating a visible-range absorption spectrum of the purple variety, they did not give any detailed explanation for the cause of the material's attractive colour. The present article provides this explanation.

Materials and methods

Two samples, representative of both colours of manganoan sugilite, were selected for this spectro-

TABLE 1. Chemical analyses of the two manganoan sugilite samples investigated. Because the electron microprobe used could not analyse for lithium, the totals do not add up to 100%. In addition, traces of Sr were detected using energy-dispersive X-ray fluorescence in both samples

Oxide (wt.%)	Purple	Pink
MnO	0.48	0.11
FeO	13.34	0.05
SiO_2	69.59	74.84
Al_2O_3	0.42	10.34
CaO	0.00	0.15
MgO	0.02	0.00
CuO	0.02	0.00
TiO_2	0.00	0.00
Cr_2O_3	0.00	0.01
Na_2O	5.68	5.94
P_2O_5	0.00	0.02
K_2O	4.84	4.62
Total	94.40	96.09

scopy study. The purple one was very darkly coloured, and it had to be thinned to make it possible to record the maximum of the visible range absorption in transmittance measurements of its spectrum. For this purpose, it was mounted using Canada balsam on a slide of Suprasil silica glass (transparent down to 200 nm, except for the additional absorption from Canada balsam). The final thickness of this sample is estimated to be 0.4 mm. The pink sample is translucent, and much thicker (about 2 mm). When examined under a microscope, both samples appeared to be polycrystalline.

The chemical composition of both samples was determined using the electron microprobe (Jeol 733 Superprobe) at the Center for Materials Research, Stanford University, Stanford, California. The results of this analysis can be found in Table 1. Both samples were also run for confirmation of these results and trace element analysis on a Spectrace 5000 energy-dispersive X-ray fluorescence spectrometer. Electron spin resonance (ESR) spectra were obtained on chips of both samples at the Chemistry Department of the California Institute of Technology.

An Hitachi U4001 UV/VIS/NIR spectrophotometer was used to record the absorption spectra of the two samples at both room and liquid-nitrogen temperatures over the range 300–850 nm (at a scan speed of 120 nm/min, and with a slit width of 2 nm). These optical spectra represent the absorption in a random direction of this polycrystalline material. No difference in colour with sample orientation was noted. The two spectra are illustrated in Fig. 1.

Results

The two room-temperature absorption spectra both have a broad region of absorption between ~450 and 600 nm, and a series of weaker, sharper absorption bands at approximately 447, 485, 498 and 537 nm. These sharper bands are found at virtually the same wavelength position in both spectra and in approximately similar proportions with the main broad band and, therefore, are probably associated with this latter band (which is the main cause of colour). In addition, both spectra display increasing absorption toward the ultraviolet. However, a detailed comparison of both spectra reveals differences, some of which can be related to the colours of these two sugilite samples:

(1) The maximum of the broad absorption band occurs at slightly different wavelengths: at approximately 560 nm in the purple sample, and at 540 nm for the pink one. This shift contributes by the elimination of more blue component from, and by the addition of more red component to the light going through the pink sample. This alone can explain its less violet, pinker colour. (2) Sharp bands present at approximately 348, 362, 412 and 418 nm, in the spectrum of purple sugilite, are absent in the spectrum of the pink sample. A very weak, broad band centred at 768 nm was noted in the spectrum of the purple sample; it too is absent from the spectrum of the pink sample. Because these absorptions are fairly weak, we do not believe that they have a significant influence on the colour. (3) The increasing absorption toward the ultraviolet starts at a higher wavelength in the pink sample. This may not be due entirely to absorption, but possibly to a larger contribution from scattering in the spectrum of the thicker, pink sample. Colour calculations done using the spectrum of the pink sample and the Galactic colour software demonstrate that even with this higher wavelength cut-off, the colour of the sample should appear pink. Therefore, whether or not this cut-off is due to absorption, it does not significantly influence the colour.

We estimate the absorption coefficient epsilon of Mn^{3+} in sugilite to be approximately 1600 (l.g.atom$^{-1}_{Mn^{3+}}$cm^{-1}) in pink sugilite, and 1700 in purple sugilite (given the uncertainties of our measurements, these two numbers are not significantly different). These values are much higher than those normally reported for Mn^{3+} in

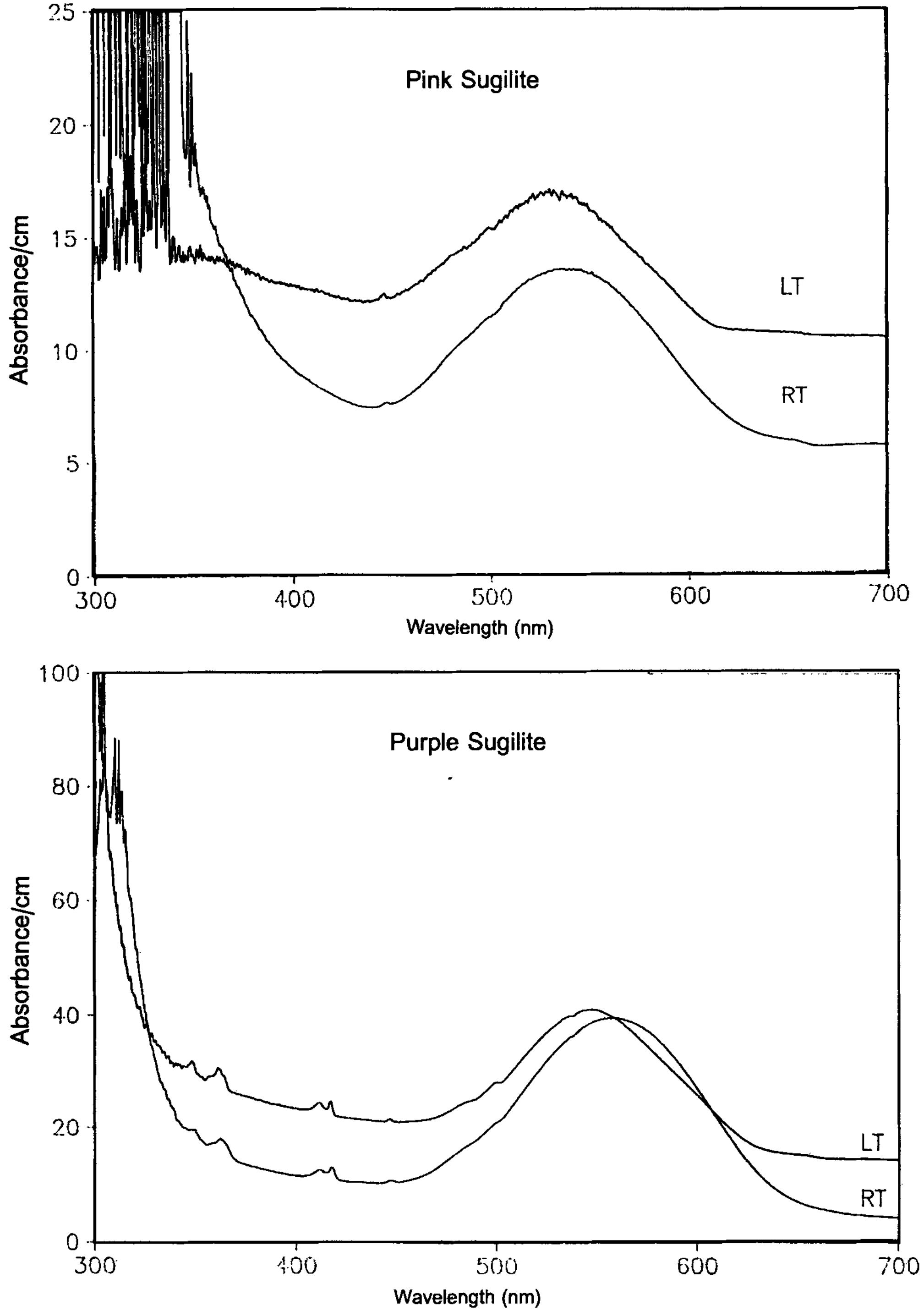

FIG. 1. Optical absorption spectra of pink (top) and purple (bottom) manganoan sugilites from the Wessels mine, South Africa, recorded at room temperature (RT) and liquid nitrogen temperature (LT).

a distorted octahedral environment, which range from approximately 20 to 300 (Smith *et al.*, 1982; Ghose *et al.*, 1986). However, a comparable value (1900) was found for Mn^{3+} in purple yoderite, reportedly because of the five-fold coordination of the Mn-site and the covalency of the Mn^{3+}-O bond (Langer *et al.*, 1982). In addition, according to Armbruster and Oberhänsli (1988), the Mn^{3+} site in sugilite is a fairly regular octahedron, whereas Mn^{3+} is generally known to occur in stabilized distorted octahedral environments (Smith *et al.*, 1982; Ghose *et al.*, 1986).

Absorption spectra obtained at liquid nitrogen temperature show a shift of the maximum of the main, broad band of about 10 nm toward lower wavelengths for both samples. Also, the absorbance at the maximum is reduced by a factor of approximately 25% compared with the corresponding room temperature spectrum.

Additionally, ESR spectra showed no Mn^{2+} superfine structure in either sample. This suggests that all Mn present is in the 3+ state, since other valence states of this ion are very rare in nature. There is virtually no resonance in the pink sample. The purple sample shows a broad absorption centred at about $g=2$ with a Δ Hpp of about 800 Gauss. This is very different from the expected Fe^{3+} spectrum, with a main resonance at about $g=4.3$. This suggests the presence of spin–spin interactions.

Discussion

We propose to assign the broad band situated between 450 and 600 nm to Mn^{3+}. This assignment is supported by the following reasons:

(1) Comparing the two optical absorption spectra with the chemical analysis data, the broad band is about 4.5 times more intense in the spectrum of the purple sugilite, which contains approximately 4.5 times more manganese. This suggests that this band is related to manganese.

(2) The attribution of the 3+ valence state to the manganese ion can be confirmed in two independent ways. First, ESR results indicate that all the manganese is present as Mn^{3+}. Second, the weak features at 447, 485, 498 and 537 nm, which are sharper at low temperature, correspond to forbidden transitions of the Mn^{3+} ion only. Also, the energy position and general shape of the absorption features are similar to those observed in other minerals coloured by Mn^{3+}, such as pink tourmaline, the piemontite variety of epidote, and red beryl (Marfunin, 1979).

The shift of the broad band from approximately 560 nm in the purple sample to 540 nm in the pink one can be explained by a change in the crystal field around the Mn^{3+} ion. The probable cause for this change can be found in the chemical analysis, which shows that the pink variety contains 10% more Al and 13% less Fe than the purple sugilite.

Cabella *et al.* (1990) described a pink, Al-rich (9.70% Al_2O_3 for the most aluminous sample), Fe-poor (0.28% Fe_2O_3), manganoan sugilite from the Cerchiara Mine in the Northern Apennines of Italy. This suggests that the presence of Al and virtual absence of Fe correlates with a pink colour for manganoan sugilite. This also reinforces that the change in Mn^{3+} crystal field is the result of a specific chemistry.

However, there are several indications that the Mn^{3+} absorption is not purely due to crystal field transitions. The shift and significant reduction of the absorption when the temperature is lowered suggests that charge transfer processes may be involved (Smith and Strens, 1976). This would help explain the unusually high extinction coefficient that we have measured.

The sharp bands at about 348, 362, 412 and 418 nm are reminiscent of sharp bands due to Mn^{2+} found at about 340, 360 and 410 nm in most minerals (Marfunin, 1979). However, we have demonstrated above that there are no indications of the presence of Mn^{2+} in our two samples. Another alternative assignment is the forbidden transitions of Fe^{3+}. For those, however, the longest wavelength absorption is located in most minerals around 440 nm; that is, at a significantly longer wavelength. A number of factors make it the most likely explanation:

(1) These sharp bands are clearly visible in the spectrum of the purple sample, which contains 13% FeO, but are absent from the spectrum of the pink samples, which contain only a trace of Fe (again, see Table 1). This points to a correlation of these absorptions with the presence of Fe.

(2) The absorption coefficients of the bands at 348, 362, 412 and 418 nm are 3.5, 5.6, 3.2 and 4.2 $\mathrm{l.g.atom}_{Fe^{3+}}^{-1}\,\mathrm{cm}^{-1}$ respectively. These values are typical for these transitions of Fe^{3+} in a distorted octahedral site (G.R. Rossman, pers. comm., 1994). Incidentally, these values would be also typical for Mn^{2+} but we have already eliminated that possibility on the basis of spectroscopic results.

(3) Although the energy positions of these transitions are atypical for Fe^{3+} in most minerals, they are similar to those measured for Fe^{3+} in the restricted class of the ring silicates (G.R. Rossman, pers. comm., 1994), to which sugilite belongs.

Therefore, we ascribe the sharp bands discussed above to Fe^{3+}. The minor broad absorption feature centred at about 768 nm is attributed to the same ion.

Conclusion

The purple and pink colours of sugilite are attributed to Mn^{3+}. The two colours are explained by two different crystal fields, resulting from distinct chemical compositions: pink sugilite is Al-rich and Fe-poor compared with the purple variety. Other potential colouring agents, in particular Fe^{3+}, do not seem to make a significant contribution. However, the unusually high coefficient of extinction, and temperature behaviour of the Mn^{3+} main absorption, leads us to believe that absorption processes that are different from crystal field transitions at an isolated ion are also involved. Fe^{3+} transitions are reported at 348, 362, 412 and 418 nm, which are significantly lower energy positions than most minerals, except for ring silicates.

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