

## ON VIOLET COLORATION OF NATURAL FLUORITE

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### INTRODUCTION

Pure  $\text{CaF}_2$  is colourless. Any colouration of fluorite is therefore related to defects (own colour) or inclusions of other phases. In nature, fluorite exhibits green, violet, blue, yellow, rose, brownish-rose, and brown colourations of various intensity. The defects causing a specific colour are well studied in most cases. For example, green colouration results from absorption of  $\text{Sm}^{2+}$  produced by radioactive irradiation converting  $\text{Sm}^{3+}$  impurities with non-local compensation of the excess charge (Feofilov 1956, Bill and Calas 1978, Chatagnon et al. 1982, Kempe et al. 2002) while blue colour is caused by a “four-band-spectra” of absorption related to Y-PC centres ( $\text{Y}^{3+}$  on a Ca site with an adjacent anion vacancy plus two electrons located near this vacancy; Bill and Calas 1978). However, the physical background of violet colouration is not as yet well understood although this kind of colouration is one of the most common types in natural fluorite.

A review of the literature shows that there are four groups of models which try to explain the violet colour: (1) inclusions of organic compounds, (2) some kind of impurity defects as  $\text{Mn}^{2+}$ ,  $\text{REE}^{3+}$ , or  $\text{REE}^{2+}$ , (3) colloids of metallic Ca formed under radioactive irradiation, (4) some kind of hole or electron centre with the charge trapped somewhere in the lattice. Because the first two models are disproved by observations (e.g., Mackenzie and Green 1971, Braithwaite et al. 1973), they will not be discussed further here.

### COLLOIDS OF METALLIC Ca

Recently, most popular seems the opinion that violet colour of natural fluorite is caused by scattering of visible light on colloidal Ca formed under radioactive irradiation (Mackenzie and Green 1971, Braithwaite et al. 1973, Bill and Calas 1978). Provided that this assumption is true, some criteria may be established which should be fulfilled in this case:

#### *1. Occurrence and optical properties*

It should be possible to produce violet colouration of synthetic fluorite by additive colouration (in Ca vapour at high temperatures) or by irradiation what is indeed observed. Note that coloration of pure  $\text{CaF}_2$  seems to be impossible, however (Görlich et al. 1961, O'Connor and Chen 1963, McLaughlan and Evans 1968, Hayes 1974, Kempe, unpublished). Synthetic coloured fluorite shows a broad absorption band at 550 nm (McLaughlan and Evans 1968, Hayes 1974). However, in natural violet fluorite the broad band absorption peaks always at

580 nm (Mackenzie and Green 1971, Braithwaite et al. 1973, Kempe et al., unpublished). In contrast, the peak position of the absorption caused by colloidal Ca should vary with particle size from 510-540 up to 580 nm with increasing size of the particles (e.g., Braithwaite et al. 1973). Colloids should also cause Tyndall scattering for larger particles what is never observed for natural samples (Braithwaite et al. 1973, Trinkler, 1997).

### *2. Behaviour at elevated temperatures*

When the temperature is raised above room temperature, an increase of the particle size is expected which should result in a shift of the absorption maximum to longer wavelength as observed for synthetic samples (Bennewitz et al. 1995). In experiments on natural samples, however, the opposite trend is observed (Braithwaite et al. 1973). Moreover, Ca colloids in fluorite are stable up to temperatures of at least 500 °C (McLaughlan and Evans 1968, Mackenzie and Green 1971). In contrast, violet colouration in natural fluorite is bleached by heating at temperatures of about 350 °C (Mackenzie and Green 1971, Braithwaite et al. 1973, Kempe et al. 2002).

### *3. Paramagnetic properties*

McLaughlan and Evans (1968) found a single EPR line with  $g=2.006$  at temperatures below 12 K in synthetic samples after irradiation at room temperature which they linked to colloid formation in the samples. No such line characteristic of violet fluorite has been identified so far during our EPR studies (Kempe et al. 2002). Summarizing, the presence of colloidal Ca in natural fluorite cannot be proved for the violet samples.

## ELECTRON DEFECTS

An alternative explanation for the appearance of violet colour is the formation of colour centres (electron or hole defects) in natural fluorite during crystal growth or radioactive irradiation. However, known defects in synthetic and natural samples cannot be taken into consideration in this context because of their different absorption properties and thermal stability (see Hayes 1974 for a review). Nevertheless, most of the characteristics described above are typical of electron defects. The known facts point most possibly to an electron defect stabilized by additional impurities as  $\text{Na}^+$  and/or  $\text{O}^{2-}$ .

## CONCLUSIONS

Violet colour is one of the most common colour types in natural fluorite. However, the colour centre causing this characteristic mineral property is not yet identified. Review of published data and first results of spectroscopic investigations point to a specific electron defect responsible for colouration. Further work is in progress to clarify the nature of the colour centre causing violet colouration in natural fluorite.

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