

LETTER TO THE EDITOR

LUMINESCENCE OF NATURAL CALCITE (CaCO_3)

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Received 9 September 1983

Recently the luminescence of Mn^{2+} in natural calcite (CaCO_3) has been reported [1]. The crystals showed a red luminescence which was ascribed to the ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ transition on the Mn^{2+} ion. In addition, an ultraviolet emission was observed which was also ascribed to the Mn^{2+} ion. It is the purpose of this letter to present a more satisfying explanation of this emission band.

The uv emission band is rather broad and shows two emission maxima, viz. at 345 and 367 nm [1]. This corresponds to an energy difference of about 1800 cm^{-1} . Such an emission band is characteristically given by the Ce^{3+} ion, the two maxima corresponding to the two levels of the $4f^1$ ground state, viz. ${}^2\text{F}_{5/2}$ and ${}^2\text{F}_{7/2}$ [2]. The Ce^{3+} ion might be present in the natural calcite crystals as an impurity.

The uv emission shows an excitation spectrum with band maxima at 313, 285 and 245 nm [1]. These correspond to $4f \rightarrow 5d$ transitions on Ce^{3+} and were also observed in the absorption spectrum of the crystals. This is not surprising since these transitions are fully allowed.

The luminescence of Ce^{3+} in ScBO_3 , which has also calcite structure, has been reported years ago [2]. The excitation spectra could be interpreted completely in view of the simple site symmetry in this lattice (distorted octahedron with D_{3d} symmetry). A comparison of the Ce^{3+} absorption bands in ScBO_3 and CaCO_3 is interesting:

| | | | | |
|-----------------|------|------|------|------|
| ScBO_3 | 28.0 | 31.2 | 36.1 | 38.5 |
| CaCO_3 | 31.9 | 35.1 | 40.8 | |

All values are in 10^3 cm^{-1} . The two lower values relate to the cubic t_{2g} components, the higher ones to the e_g components [2]. Note that the bands for Ce^{3+} in CaCO_3 are at about 4000 cm^{-1} higher energy than in ScBO_3 . This is probably related to different crystal fields, since there is less space for Ce^{3+}

($r = 1.15 \text{ \AA}$) in ScBO₃ ($r_{\text{Sc}^{3+}} = 0.745 \text{ \AA}$) than in CaCO₃ ($r_{\text{Ca}^{2+}} = 1.00 \text{ \AA}$), where the ionic radii are taken from ref. [3].

The uv emission can, therefore, be ascribed to Ce³⁺. It is interesting to note that the Ce³⁺ excitation bands occur also in the Mn²⁺ excitation spectrum [1]. This shows that energy transfer from Ce³⁺ to Mn²⁺ occurs. In fact, Botden [4] already stated "that CaCO₃ activated with manganese cannot be excited by uv radiation, but CaCO₃ activated with lead, thallium or cerium and manganese shows an orange-red manganese luminescence under uv radiation at room temperature". X-ray irradiation may change the cerium valency. This explains the result reported in [1] that the uv excitation bands disappear after X-ray irradiation.

Using the data in ref. [1] it is possible to discuss the Ce³⁺ → Mn²⁺ transfer in CaCO₃ in more detail. It is possible [5] to calculate the critical distance R_c for electric dipole-dipole interaction from

$$R_c^6 = 0.63 \times 10^{28} Q_A E^{-4} \int f_s(E) F_A(E) dE.$$

Here Q_A is the absorption cross section of the acceptor (Mn²⁺), given by $Q_A = 4.8 \times 10^{-16} P_A$, where P is the oscillator strength; E is the energy of maximum spectral overlap; the integral presents the spectral overlap [6]. The latter is calculated from the spectral data in ref. [1] and amounts to 1.5 eV^{-1} . Especially the overlap of the Ce³⁺ emission band and the Mn²⁺ excitation band at 359 nm is very favourable. for P_A we took 0.5×10^{-6} [7]. This yields $R \approx 5.0 \text{ \AA}$. If transfer by electric dipole-dipole interaction spans this distance, possible contributions by exchange interaction cannot be of great importance.

Using the crystallographic data of CaCO₃ (calcite) and $R_c \approx 5 \text{ \AA}$, it is found that the Ce³⁺ ion is able to transfer to Mn²⁺ ions on the 8 nearest-neighbour calcium sites. Here a statistical distribution is assumed and Ce³⁺ → Ce³⁺ transfer neglected.

From the analytical results the Mn mole fraction is found to be 2×10^{-3} . The probability that a Ce³⁺ ion has no Mn²⁺ ions on these 8 sites is $0.998^8 = 0.984$. This predicts that Ce³⁺ excitation is followed by emission consisting of 98.4% Ce³⁺ emission and 1.6% Mn²⁺ emission. Since the Mn²⁺ excitation bands of Ce³⁺ are one order of magnitude more intense than those of Mn²⁺ in the Mn²⁺ excitation spectrum [1], the Ce³⁺ ions give an absorbance which is about 600 times as large as that of the Mn²⁺ ions. This explains why the absorption spectrum of the crystals shows only Ce³⁺ and no Mn²⁺ transitions [1]. Since the oscillator strengths of the two ions differ about 10^6 [7], the Ce³⁺ mole fraction in the crystals is estimated to be $600 \times 10^{-6} \times 2 \times 10^{-3} \approx 10^{-6}$. Such a low amount of Ce³⁺ can easily be present in natural crystals. The results show that the presence of a small amount of strongly absorbing and emitting ions can have drastic influence on the luminescence spectra.

References

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