Luminescence Spectra of Mn^{2+} Doped in Langbeinites

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Luminescence data for 6 manganese doped langbeinites, $A_2^+B_2^{2+}(SO_4)_3$, are reported. They are consistent with octahedral symmetry of the impurity center (substitutional in B site), although for the host lattice the B site is known to show three-fold axial (distorted octahedral) symmetry only. In accordance with previous conclusions from EPR data the luminescence parameters indicate structural relaxation in comparison to undoped langbeinites.

Langbeinites are a group of substances of the general composition $A_2B_2(SO_4)_3$, where A denotes a monovalent and B a divalent cation as in the mineral $K_2Mg_2(SO_4)_3$, after which they are named. In their high temperature phase they crystallize isomorphously in the cubic space group $P2_13$, with the cations as B(1)–A(1)–A(2)–B(2) in crystallographically nonequivalent sites along the three-fold [111] symmetry axis [1–5]. Other divalent cations can be incorporated substitutionally in B sites. Using that possibility, we have studied in a previous paper Mn^{2+} doped langbeinites by means of electron paramagnetic resonance (EPR) in order to gain information on these centers [6]. Both nonequivalent B sites were found to be accepted by Mn^{2+}, though the more spacious one seems to be clearly preferred. There is a correlation of EPR parameters with the ratio of ionic radii $Q = r_B/r_A$ of the host ions which probably is due to local structural relaxation. According to structure refinements of (undoped) langbeinites [1–5], the B sites in question are characterized by a six-fold oxygen coordination, the O ligands being arranged in a somewhat distorted octahedron around the central B ion. Depending on whether the Mn^{2+} ion is smaller or larger than the B type host ions, relaxation is suspected to reduce or increase the distortion, respectively, retaining, however, the three-fold symmetry with respect to the above-mentioned [111] axis.

Supplementary information concerning the proposed relaxation model may be gained from optical measurements, which to our knowledge have not yet been carried out with Mn^{2+} doped langbeinites. Therefore the present note is intended to report some results obtained by luminescence spectroscopy on 6 langbeinites, namely Rb-Mg, K-Mg, K-Zn, Rb-Cd, Tl-Cd and NH_4-Cd langbeinite.

Single crystals were prepared as described previously [2, 6, 7–11]. Specimens of at least 1.5 mm edge length were chosen and polished for measurement. Luminescence spectra were recorded with an Aminco-Bowman spectrofluorometer in the 200 ... 800 nm range of wavelengths, with the excitation beam directly normally onto a crystal face.

Figure 1 represents a typical excitation spectrum, as similarly obtained with all the langbeinites studied. Those spectra are in full agreement with the expectations for the case of an undisturbed octahedral site symmetry. Assuming regular octahedral symmetry, the peaks can be assigned by means of Tanabe-Sugano diagrams [12, 13]. Accordingly, the narrowest peak is attributed to a transition which depends as little as possible on the ligand field strength, which means that the peak at $\approx 25\,000$ cm^{-1} (400 nm) is probably due to the ${}^6A_{1g} \rightarrow {}^4A_{1g}/{}^4E_g$ transition. From that starting point the assignment of the peaks at lower and higher wavenumbers follows as given in Table 1. All peaks observed can be related to just one Mn^{2+} center of octahedral symmetry, i.e. there is no obvious hint at a second center.

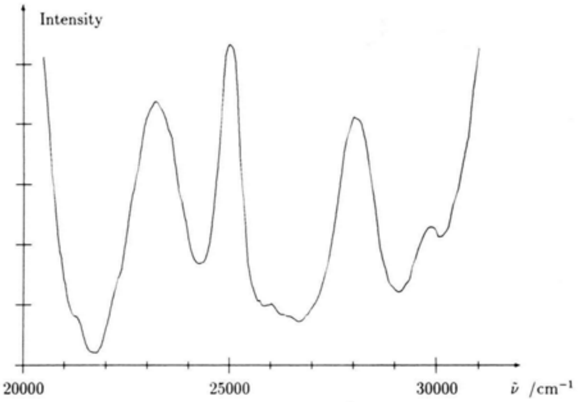

Fig. 1. Excitation spectrum of Mn^{2+} doped Rb-Mg langbeinite (intensity/a.u. against wavenumber $\tilde{\nu}$/cm^{-1}). Emission wavelength $\lambda_E = 569$ nm. (The intensity in outer parts of the spectrum is due to scattered light.)

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Table 1. Luminescence excitation wavelengths λ, emission wavelengths λ_E, and parameters B and Dq as derived from the spectra, for the Mn^{2+} doped langbeinites.

Langbeinite		Excitation wavelengths λ (nm) [a]					λ_E	B	Dq
A	B	1	2	3	4	5	(nm)	(cm^{-1})	(cm^{-1})
Rb	Mg	469 (2)	431 (2)	400 (2)	358 (2)	335 (2)	569 (3)	772 (4)	≈736
K	Mg	470 (3)	428 (3)	401 (3)	357 (3)	336 (3)	≈578	770 (6)	≈702
K	Zn	455 (3)	423 (3)	400 (3)	359 (3)	–	557 (6)	772 (6)	≈650
Rb	Cd	473 (2)	424 (2)	400 (2)	356 (2)	334 (2)	554 (4)	772 (4)	≈679
Tl	Cd	–	420 (4)	400 (4)	353 (4)	–	556 (5)	772 (8)	≈614
NH_4	Cd	475 (2)	430 (2)	402 (2)	357 (2)	337 (2)	554 (5)	768 (4)	≈708

[a] Numbering of transitions:

No.	1	2	3	4	5
Trans.	$^6A_{1g} \rightarrow {}^4T_{1g}$	$^6A_{1g} \rightarrow {}^4T_{2g}^a$	$^6A_{1g} \rightarrow {}^4A_{1g}/{}^4E_g$	$^6A_{1g} \rightarrow {}^4T_{2g}^b$	$^6A_{1g} \rightarrow {}^4E_g$

Table 1 summarizes also some further parameters. The emission wavelength λ_E was separately determined from emission spectra. The Racah parameter B was obtained according to [12]

$$\Delta({}^4G - {}^6S) = 10\,B + 5\,C\,,$$

where the free ion terms ^6S and ^4G correspond to the terms $^6A_{1g}$ and $^4A_{1g}/{}^4E_g$, respectively, in the case of octahedral ligand field symmetry, and the Racah parameter C can be put $C = 4.48 \cdot B$ [12]. The ligand field strength parameter Dq was then read from the Tanabe-Sugano diagram in consideration of the difference between $^4T_{2g}^a$ and $^4A_{1g}/{}^4E_g$ states.

The values of B and λ_E are practically unaffected by the langbeinite composition. The approximate constancy of B indicates that roughly the same space is available for the Mn^{2+} d-electrons in spite of being placed in crystals of different composition. The constancy of λ_E points in the same direction. Thus the conclusion appears that the assumed structural relaxation leads to an octahedral arrangement of the oxygen ligands where the relaxed Mn-O distances are essentially governed by the size of the central probe ion Mn^{2+}. On the other hand, the Dq values show a rather broad scatter. These values cannot be arranged as to reveal any correlation to the radii of host and impurity ions. The scatter may result from the involvement of excited states in the determination of Dq. Those states are possibly more sensitive to the crystallographic fine structure than the ground states.

Summing up, the luminescence data corroborate the model derived from the EPR results concerning the structural relaxation around Mn^{2+} centers in langbeinites in so far as the (relaxed) distances appear to be determined by the radius of the impurity ion. Since the spectra are explicable in terms of apparent O_h symmetry, however, optical spectroscopy of Mn^{2+} is obviously too insensitive to probe the distortion of the ligand arrangement which was ascertained by EPR results, as it is also unsuitable for resolving the presumed contributions from the two different centers.

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