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NOTES

Luminescence of Barium Magnesium Sulfate

The luminescence of V^{5+}, Ce^{3+}, Eu^{3+}, Tb^{3+}, W^{6+}, and Pb^{2+} in barium magnesium sulfate, $BaMg(SO_4)_2$, is reported. Results are discussed in relation to the crystal structure and the Eu^{2+} luminescence in this compound reported earlier.

Recently Ryan et al. (*1*) have reported the existence of a compound $BaMg(SO_4)_2$ and the remarkable luminescence of the Eu^{2+} ion in this host lattice. The emission spectrum at low temperatures consists of a number of sharp lines that were attributed to transitions from the $^6P_{5/2}$ and $^6P_{7/2}$ levels to the $^8S_{7/2}$ level within the $4f^7$ configuration and their phonon replicas. The excitation spectrum of this luminescence shows transitions to the seven ^7F_J levels of the Eu^{3+} core imposed on top of the lowest crystal field state of the additional $5d$ electron. This corresponds to weak exchange interaction between the $4f^6$ and $5d$ electrons. To explain these phenomena the crystal field at the Eu^{2+} site in $BaMg(SO_4)_2$ should be weak and the degree of covalency high (*1*). We have recently made a crystal structure proposal for $BaMg(SO_4)_2$ from powder data (*2*). $BaMg(SO_4)_2$ is isomorphous with the waterfree alums (*3*). This implies 12 coordination for Ba^{2+} in a hexagonally close-packed way and 6 coordination for Mg^{2+} in a trigonal prism. The structure contains layers consisting of sulfate tetrahedra separated alternately by Ba^{2+} layers and Mg^{2+} layers. It is the purpose of this paper to report on the luminescence of some other activators in this lattice and to explain the reported Eu^{2+} luminescence from the crystal structural data.

Samples were prepared as described before (*2*). The performance of the optical measurements was similar to those in earlier papers (*4*).

The following activators showed efficient luminescence at room temperature: V^{5+} (compensated with Al^{3+}, Cr^{3+}, or La^{3+}), Ce^{3+} and Tb^{3+} (compensated with P^{5+}), W^{6+}, and Pb^{2+}. It was very hard to introduce europium in the trivalent state, but we obtained some samples with characteristic Eu^{3+} emission using V^{5+} compensation. The Ce^{3+} and Eu^{3+} ions were used to investigate the crystal-field at the Ba^{2+} site of $BaMg(SO_4)_2$. The Pb^{2+} ion was applied to study the influence of exchange on the energy levels. No luminescence was observed for W^{6+} in the isomorphous $KAl(SO_4)_2$. Table I surveys the results obtained at room temperature. These are not strikingly different at lower temperatures.

The Eu^{3+} Ion

In addition to weak emission from the $^5D_1$ level the Eu^{3+} ion in $BaMg(SO_4)_2$ shows the usual red emission from the $^5D_0$ level. There is one line corresponding with the $^5D_0$–$^7F_1$ transition (595 nm) and two lines corresponding with the $^5D_0$–$^7F_2$ transition (616 and 619 nm). The $^5D_0$–$^7F_0$ line is missing. These numbers agree with the site symmetry D_3 of the Ba^{2+} site in our structure proposal.

The Ce^{3+} Ion

The emission and excitation band of the luminescence of Ce^{3+} in $BaMg(SO_4)_2$ lies at remarkably short wavelengths in comparison with those in other Ce^{3+}-activated oxides (*5*, *6*). As argued in Ref. (*6*) this is strong evidence for a weak crystal field at the Ce^{3+} ion. The variation of the Ce^{3+} emission in oxides is also impressive if one considers $BaMg(SO_4)_2{:}Ce$ with emission maximum at about 32 500 cm^{-1} as the higher-energy limit and $Y_3Al_5O_{12}{:}Ce$

TABLE I

Luminescence Properties of Some Activators in $BaMg(SO_4)_2$ at Room Temperature

Composition (activator concentration 1 at. %)	Maximum of emission band (nm)	Maximum of excitation band (nm)
$BaMg(SO_4)_2$–W^{6+}	505	290
$BaMg(SO_4)_2$–Pb^{2+}	350	≃215
$BaMg(SO_4)_2$–V^{5+}, Al^{3+}	530[a]	325[a]
$BaMg(SO_4)_2$–Ce^{3+}, P^{5+}	305	270
$BaMg(SO_4)_2$–Tb^{3+}, P^{5+}	b	≃250
$BaMg(SO_4)_2$–Eu^{3+}, V^{5+}	595, 616, 619[c]	—

[a] Similar results for La^{3+} or Cr^{3+} compensation.

[b] Characteristic emission from $^5D_3$ and $^5D_4$ level.

[c] Also some weak emission from $^5D_1$ level.

with about 18 200 cm^{-1} as the lower-energy limit (*6*).

The Pb^{2+} Ion

The emission and excitation band of Pb^{2+} in $BaMg(SO_4)_2$ is very similar to those in $BaSO_4$ and $CaSO_4$ (*7*), but they are situated at somewhat higher energy in the double sulfate. Due to the insensitivity of our apparatus below 250 nm the values of the excitation band are not very accurate.

The Eu^{2+} emission

The hypothesis on the crystal structure of $BaMg(SO_4)_2$ made by Ryan et al. (*1*) to explain the Eu^{2+} luminescence in this compound can now be tested. All our results indicate indeed a weak crystal field at the large cation site: the short wavelength absorption of Ce^{3+}, twelve coordination and the probably long Eu^{2+}–O^{2-} distances. A great degree of covalency at this site can be imagined, if one realizes the structure of the compounds. Sulfate layers are surrounded on one side by Ba^{2+} layers and on the other side by Mg^{2+} ions. Consequently the sulfate layers will be polarized and electronic charge is removed from the Ba^{2+} layer to the sulfate layer. A great degree of covalency results in weak exchange interaction between the $4f^6$ and $5d$ electrons of Eu^{2+}. This in turn should also be true for the $6s$ and $6p$ electrons in the excited state of the Pb^{2+} ion. Weak exchange should lift the position of the emitting and absorbing $^3P_1$ level. This corresponds with the observed relatively short-wavelength absorption and emission of the Pb^{2+} ion.

The W^{6+} Emission

It is also possible to introduce W^{6+} in the lattice (on sulfate sites). The tungstate tetrahedron should experience a strong, trigonal field in this structure. The luminescence of this group in $BaMg(SO_4)_2$ is not unusual, but the emission and excitation bands are at long wavelengths compared with the tungstate emission in the alkaline earth sulfates (8). At the same time the quenching temperature of the tungstate luminescence in the mixed sulfate is high, 435°K. The value for $CaWO_4$ is 410°K and for $SrWO_4$ and $BaWO_4$ much lower; for $MgWO_4$ (with tungstate octahedra) 460°K has been reported (*9*). The difference between tetrahedral tungstate luminescence in the double sulfate and the alkaline earth tungstates (or sulfates) is not easy to explain. Two factors may be of importance. The trigonal field at the tetrahedron in $BaMg(SO_4)_2$ will result in splitting of the regularly tetrahedral levels. As a consequence the energy difference between the highest filled and the lowest empty molecular orbital will decrease, so that excitation and emission bands shift to lower energies. The relatively high quenching temperature of the luminescence may be due to the nature of the surroundings of the tungstate tetrahedron. On one side the Mg^{2+} ions represent a stiffer surroundings than the larger alkaline–earth ions; on the other side the tungstate oxygen ion sees sulfate oxygen ions which will also restrict expansion of the tungstate group upon expansion. Due to the structural arrangement the Ba^{2+} ions do not play an important role in counteracting an expansion of the tungstate tetrahedron. Restricted expansion implies a higher quenching temperature, in agreement with our observation.

Note, finally, that the tungstate group in $KAl(SO_4)_2$ does not luminesce. The waterfree alum has $c/a = 1.7$, the double sulfate 1.5. The stronger extension of the alum in the *c*-direction is expected to increase the distances in this direction, so that the arguments mentioned above are no longer valid.

The V^{5+} Emission

The vanadate emission does not depend on the way in which the V^{5+} ion (on S^{6+} sites) is charge-compensated. This indicates that there is no association of the vanadium ion and its compensator as observed in other sulfates (*4*). The yellow emission of the vanadate group is efficient and its quenching temperature is far above room temperature.

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G. Blasse
G. P. M. van den Heuvel
J. Stegenga

Physical Laboratory
University of Utrecht
Sorbonnelaan 4, Utrecht
Netherlands

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