The Luminescence Spectra of Triply-ionized Rare Earths in the Calcination Products of Some Magnesium Compounds

By Eiichi IWASE and Seijiro NISHIYAMA

(Received May 14, 1963)

According to Tomaschek,[1] the luminescence spectra of samarium(III) ions embedded in the matrices of magnesium oxide, which are derived from the thermal treatment of magnesia usta, magnesium sulfate and magnesium chloride, are different from one another, although these matrices have the same X-ray diffraction diagram.

From the chemical point of view, the thermal decomposition of magnesium compounds does not always give rise to a simple and high-quality magnesium oxide, and the few fragments of the starting magnesium compounds remaining in the calcination products may be expected, in some cases, to have a remarkable effect on the luminescence spectra of the triply-ionized rare earths embedded therein. These effects would be detectable in variations of relative intensity, spectral position and sharpness of the luminescence bands. Therefore, measurements have been made of the luminescence spectra of the europium(III), terbium(III), and dysprosium(III) as well as of the samarium(III) ions embedded in calcination products derived from three kinds of magnesium compounds. This paper will present the experimental results obtained and some interpretations relating to them.

Experimental

High-quality crystals of $Mg(NO_3)_2\cdot 6H_2O$, $MgSO_4\cdot 7H_2O$ and $MgCl_2\cdot 6H_2O$ are soaked with a nitrate solution of one of the rare earths just mentioned, and then subjected to a calcination at about 900°C for 30 min. Some portions of these calcination products are then further heated in a flame of town gas mixed with oxygen at about 1800°C for 5 min. The concentration of the rare earth added is made to be 0.1 % of the matrix. The excitation to the luminescence is done in a small Urbain tube by cathode-ray bombardment at room temperature, and the luminescence thus yielded is spectrographically investigated by employing the glass-prism spectrograph of Feuss.

Results and Discussion

Figures. 1—4 are the schematic representations of luminescence spectra of, respectively, the samarium(III), europium(III), terbium(III) and dysprosium(III) ions which are embedded in the calcination products derived from $Mg(NO_3)_2\cdot 6H_2O$, $MgSO_4\cdot 7H_2O$ and $MgCl_2\cdot 6H_2O$ at 900 and 1800°C. The most intense bands in each of the luminescence spectra are shown in Table I. Comparing the results obtained on the matrix calcined at 900°C with those calcined at 1800°C, there will be found either a simple displacement of the band of maximum intensity or a simple interchange of intensity with another band. The former situation is

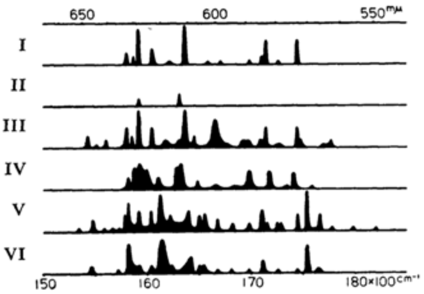
---

[1] R. Tomaschek and O. Deutschbein, *Ann. Physik*, [5] 16, 943 (1933); R. Tomaschek, *Acta Phys. Polon.*, 5, 405 (1936).

TABLE I. THE MOST INTENSE LUMINESCENCE BANDS OF TRIPLY-IONIZED RARE EARTHS EMBEDDED IN CALCINED MAGNESIUM COMPOUNDS

Starting matrix	Calcination temp., °C	Sm^{3+} cm^{-1}	Eu^{3+} cm^{-1}	Tb^{3+} cm^{-1}	Dy^{3+} cm^{-1}
$Mg(NO_3)_2\cdot 6H_2O$	900	16370	16750	17830 18310 18360	16830
	1800	16300	16750	18360	16840 17100
$MgSO_4\cdot 7H_2O$	900	16360	16750	18460	17310
	1800	16320	16260	18020 22750 23580 23710	16850
$MgCl_2\cdot 6H_2O$	900	17540	16750	18390	17360
	1800	16140	16180 16760	18260	16830

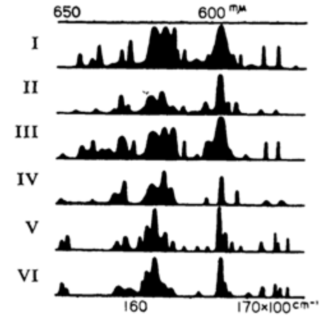
Sm^{3+}



			Number of bands observed
I	$Mg(NO_3)_2\cdot 6H_2O$	900°C	13
II	$Mg(NO_3)_2\cdot 6H_2O$	1800°C	2
III	$MgSO_4\cdot 7H_2O$	900°C	22
IV	$MgSO_4\cdot 7H_2O$	1800°C	15
V	$MgCl_2\cdot 6H_2O$	900°C	27
VI	$MgCl_2\cdot 6H_2O$	1800°C	18

Fig. 1

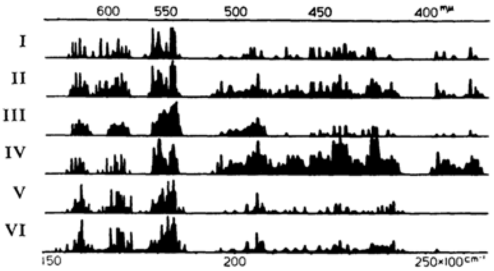
Eu^{3+}



			Number of bands observed
I	$Mg(NO_3)_2\cdot 6H_2O$	900°C	17
II	$Mg(NO_3)_2\cdot 6H_2O$	1800°C	14
III	$MgSO_4\cdot 7H_2O$	900°C	18
IV	$MgSO_4\cdot 7H_2O$	1800°C	12
V	$MgCl_2\cdot 6H_2O$	900°C	20
VI	$MgCl_2\cdot 6H_2O$	1800°C	18

Fig. 2

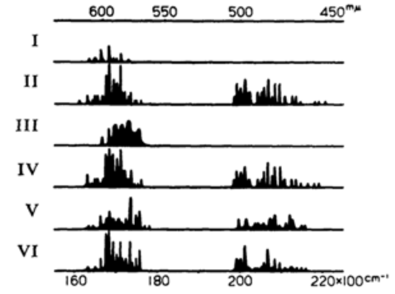
Tb^{3+}



			Number of bands observed
I	$Mg(NO_3)_2\cdot 6H_2O$	900°C	56
II	$Mg(NO_3)_2\cdot 6H_2O$	1800°C	83
III	$MgSO_4\cdot 7H_2O$	900°C	53
IV	$MgSO_4\cdot 7H_2O$	1800°C	75
V	$MgCl_2\cdot 6H_2O$	900°C	68
IV	$MgCl_2\cdot 6H_2O$	1800°C	68

Fig. 3

Dy^{3+}



			Number of bands observed
I	$Mg(NO_3)_2\cdot 6H_2O$	900°C	8
II	$Mg(NO_3)_2\cdot 6H_2O$	1800°C	40
III	$MgSO_4\cdot 7H_2O$	900°C	6
IV	$MgSO_4\cdot 7H_2O$	1800°C	36
V	$MgCl_2\cdot 6H_2O$	900°C	28
VI	$MgCl_2\cdot 6H_2O$	1800°C	32

Fig. 4

seen in the case of the samarium(III) luminescence in the $Mg(NO_3)_2 \cdot 6H_2O$-derived and $MgSO_4 \cdot 7H_2O$-derived matrices, while the latter situation is seen in the cases of the samarium(III) luminescence in the $MgCl_2 \cdot 6H_2O$-derived matrix, the europium(III) luminescence in the $MgSO_4 \cdot 7H_2O$-derived matrix, the terbium(III) luminescence in the $MgCl_2 \cdot 6H_2O$-derived matrix and the dysprosium(III) luminescence in the $MgSO_4 \cdot 7H_2O$-derived as well as the $MgCl_2 \cdot 6H_2O$-derived matrices. In some cases, circumstances are more complicated and a variation in the number of bands with the maximum intensity is seen. For instance, in the case of the terbium(III) luminescence given by the $Mg(NO_3)_2 \cdot 6H_2O$-derived matrix, one of three bands having equal maximum intensity remains unchanged in its intensity, while the other two are weakened. Thus, the bands with maximum intensity decrease in number. On the other hand, an increase in the number of bands with maximum intensity is seen, for instance, in the cases of the europium(III) luminescence given by the $MgCl_2 \cdot 6H_2O$-derived matrix and of the dysprosium(III) luminescence given by the $Mg(NO_3)_2 \cdot 6H_2O$-derived matrix, where the original band of maximum intensity is displaced and another band is intensified up to an intensity equal to that of the original one, while in the terbium(III) luminescence given by the $MgSO_4 \cdot 7H_2O$-derived matrix, the original band of maximum intensity is weakened and the other four bands tend to have an intensity equal to that of the original band. Thus, the bands of maximum intensity increase in number.

On the right of Figs. 1—4 are indicated the total number of observed bands of samarium(III), europium(III), terbium(III) and dysprosium(III) ions. When the calcination-temperature is elevated, the total number of bands of samarium(III) and europium(III) ions decreases on the contrary, that of terbium(III) ions increases with the exception of the case of the $Mg(NO_3)_2 \cdot 6H_2O$-derived matrix. Here the total number of bands remains almost unchanged. In the case of the luminescence of dysprosium(III) ions, the total number of bands increases when the calcination temperature is raised.

Generally speaking, calcination at a different temperature causes a comparatively small change in the total number of luminescence bands given by the $MgCl_2 \cdot 6H_2O$-derived matrix.

So far as the matrix calcined at 900°C is concerned, the total number of observed luminescence bands of the triply-ionized rare earths embedded in the $MgCl_2 \cdot 9H_2O$-derived matrix is much larger than in the $Mg(NO_3)_2 \cdot 6H_2O$-derived and $MgSO_4 \cdot 7H_2O$-derived matrices.

When the samarium(III), europium(III), terbium(III) and dysprosium(III) ions embedded in the matrices of magnesium compounds calcined at 900°C are subjected to further heat treatment at 1800°C, the total intensity of luminescence is changed. It is interesting to note that the magnitude of the intensity-variation of luminescence can be arranged in the sequence of increasing atomic number of these rare earths; the most marked decrease in the total intensity of luminescence is effected for samarium(III) ions, whereas the most marked increase is for dysprosium(III) ions. For europium(III) and terbium(III) ions a moderate decrease and a moderate increase in the total intensity of luminescence are observed respectively.

As the result of the elevation of the calcination temperature, the relative intensity of luminescence bands appearing side by side in the spectrum is sometimes reversed in order. For the europium(III) luminescence, this is the case with the band-couple of 15880 and 15950 cm^{-1} in the matrix derived from $Mg(NO_3)_2 \cdot 6H_2O$ and with those of 15360 and 15400 cm^{-1}, as well as with 15840 and 15920 cm^{-1} in the matrix derived from $MgCl_2 \cdot 6H_2O$. For the terbium(III) luminescence a similar reversal of intensity is observed in the bands of 15920, 16000 and 16060 cm^{-1} in the matrix derived from $Mg(NO_3)_2 \cdot 6H_2O$.

In the case of $Mg(NO_3)_2 \cdot 6H_2O$, thermal conversion to magnesium oxide goes forward so smoothly that the luminescence spectrum of each of the triply-ionized rare earths embedded in magnesium oxide is obtained in its pure form. As was expected, the thermal decomposition to magnesium oxide does not proceed easily for $MgSO_4 \cdot 7H_2O$. Turbidimetric analyses of SO_4^{2-} as barium sulfate sol (Table II, upper line) show that about 2/3 of the starting material is decomposed to magnesium oxide by calcining at 900°C for 30 min. in an electric furnace and that about 1/4 of the sulfate component still remains in a product subjected to further heating in a flame of town gas mixed with oxygen at 1800°C for 5 min. Due to the sulfate component remaining in the matrix calcined at 900°C, a number of characteristic diffuse bands and their conglomeration are

TABLE II. EXAMPLES OF CHEMICAL ANALYSES OF REMAINING COMPONENTS IN CALCINED PRODUCTS

Starting substances	900°C 30 min.	1800°C 5 min.
$MgSO_4 \cdot 7H_2O$	25.66%	19.52%
$MgCl_2 \cdot 6H_2O$	0.000147	0.000038

seen. When further decomposition occurs following heat treatment at 1800°C, the feature of the luminescence spectrum approaches that in pure magnesium oxide. Although the thermal decomposition to magnesium oxide is readily obtainable with $MgCl_2 \cdot 6H_2O$, the luminescence spectrum of each of the triply-ionized rare earths embedded therein has an appearance considerably different from the luminescence spectrum obtained in the $Mg(NO_3)_2 \cdot 6H_2O$-derived matrix; these rare earth ions give intense and sharp luminescence bands peculiar to the respective chloride-derived matrix. Examples of turbidimetric analyses as silver chloride sol (Table II, lower line) show 147 p.p.m. of chlorine content for a product calcined at 900°C for 30 min. and 38 p.p.m. of chlorine content for that calcined at 1800°C for 5 min. The quantity of chlorine ions existing in the matrix corresponds to about 64 and 17 mol. % of that of the rare earth ions respectively. It should be mentioned that even such a minute quantity of chlorine ions found in the matrix would have quite remarkable effects over the whole luminescence spectrum of the rare earth ions existing therein.

If it can be assumed that the luminescence spectrum of each of the triply-ionized rare earths embedded in either the $MgSO_4 \cdot 7H_2O$-derived or $MgCl_2 \cdot 6H_2O$-derived matrix is composed of two kinds of bands (one, the kind of bands observed in pure magnesium oxide and the other, the kind of bands characteristic of the matrix with either a sulfate or chloride component remaining therein), the composition of the luminescence spectrum, as well as the mixing ratio of these two kinds of luminescence bands, would be such as shown in Table III.

Table IV gives the frequency of some principal luminescence bands of samarium(III), europium(III), terbium(III) and dysprosium(III) ions, which is considered to be inherent in the matrices derived from $MgSO_4 \cdot 7H_2O$ and $MgCl_2 \cdot 6H_2O$ by the calcination at 900°C.

TABLE III. MIXING RATIO OF BANDS CHARACTERISTIC OF MAGNESIUM SULFATE- OR CHLORIDE-DERIVED MATRIX AND THOSE DUE TO PURE MAGNESIA IN LUMINESCENCE SPECTRUM OF TRIPLY-IONIZED RARE EARTH

Starting matrix	Sm^{3+}	Eu^{3+}	Tb^{3+}	Dy^{3+}
$MgSO_4 \cdot 7H_2O$	11/11	9/9	16/37	4/2
$MgCl_2 \cdot 6H_2O$	17/10	12/8	29/39	14/14

TABLE IV. PRINCIPAL LUMINESCENCE BANDS OF TRIPLY-IONIZED RARE EARTH CHARACTERISTIC OF THE SULFATE-DERIVED AND CHLORIDE-DERIVED MATRICES

(Calcination temp. 900°C)

Starting matrix	Sm^{3+} cm^{-1}	Eu^{3+} cm^{-1}	Tb^{3+} cm^{-1}	Dy^{3+} cm^{-1}
$MgSO_4 \cdot 7H_2O$				16990
	16460	15520	18150	17150
	16640	15700	18460	17310
		15980		17560
$MgCl_2 \cdot 6H_2O$	16130	16050	16010	17360
	17540	16100	18090	
		16180	18260	

Summary

(i) The luminescence spectra of samarium(III), europium(III), terbium(III) and dysprosium(III) ions embedded in the calcination products of $Mg(NO_3)_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$ and $MgCl_2 \cdot 6H_2O$ have been studied under excitation by cathode-ray bombardment at room temperature. The calcination of these ions was carried out either at about 900°C for 30 min. or by further heating at about 1800°C for 5 min.

(ii) The luminescence spectrum of each of the rare earth ions in magnesium oxide matrix was obtained in its pure form in the case of the calcination products derived from $Mg(NO_3)_2 \cdot 6H_2O$. A number of distinguishing diffuse luminescence bands were observed arising from the sulfate component remaining in the calcination products derived from $MgSO_4 \cdot 7H_2O$. Calcination products derived from $MgCl_2 \cdot 6H_2O$ had a composition very near that of magnesium oxide and contained only a small amount of chlorine. When the triply-ionized rare earths here investigated were embedded in these calcination products, several intense and sharp luminescence bands were found which cannot be ascribed to those observed in pure magnesium oxide, but presumably result from their chlorine content.

(iii) The luminescence spectra of these triply-ionized rare earths embedded in the matrices derived from the calcination of $MgSO_4 \cdot 7H_2O$ and $MgCl_2 \cdot 6H_2O$ were considered to be constituted of the bands observed in the matrix of pure magnesium oxide and those characteristic of a matrix containing either a sulfate- or chloride-component. The frequencies of some of the principal bands characteristic of the presence of sulfate- and chloride-components have been given for each of the triply-ionized rare earths investigated here.

(iv) As to the intensity of the luminescence of samarium(III), europium(III), terbium(III) and dysprosium(III) ions embedded in the matrices of calcined magnesium compounds, the magnitude of variation arising from heat treatment at elevated temperatures may be arranged

in the order of rare earth ions with increasing atomic numbers 62∼66, the most marked decrease being seen in the luminescence of samarium(III) ions with the smallest atomic number (62), and the most marked increase, in that of dysprosium(III) ions with the largest atomic number (66).

The Institute of Physical and
Chemical Research
Bunkyo-ku, Tokyo