

THE LUMINESCENCE OF YTTRIA STABILIZED ZIRCONIA DOPED WITH Bi_2O_3

G. Blasse and Hao Zhiran*

Physical Laboratory, State University Utrecht
P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

and

A.J.A. Winnubst and A.J. Burggraaf
Twente University of Technology
Department of Chemical Engineering
Laboratory for Inorganic Chemistry and Materials Science
P.O. Box 217, 7500 AE Enschede, The Netherlands

(Received May 17, 1984; Communicated by A. W. Sleight)

ABSTRACT

Yttria stabilized zirconia doped with Bi_2O_3 shows an efficient luminescence due to the Bi^{3+} ions. Two luminescent centres were observed which are ascribed to BiO_8 and BiO_7 groups.

Introduction

Recently Winnubst and Burggraaf [1] described a preparation method of monophasic yttria-stabilized zirconia doped with Bi_2O_3 ($\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Bi}_2\text{O}_3$). This material is a solid electrolyte which exhibits oxygen ion conduction at elevated temperatures and can be used in oxygen sensors for the regulation of combustion processes and in oxygen pumps [see ref.1 and literature cited in ref.1].

In the course of our studies on the luminescence of the Bi^{3+} ion in oxides [ref.2] we investigated also samples of yttria-stabilized zirconia doped with Bi_2O_3 . Results are reported in this paper. We have found that the Bi^{3+} ion luminesces efficiently in yttria stabilized zirconia and that there are mainly two luminescent centres present. The latter observation is discussed in connection with the defect chemistry of stabilized zirconia.

* On leave of absence from Changchun Institute of Physics, Chinese Academy of Sciences, Changchun, Peoples Republic of China.

Experimental

Samples were prepared as described in ref.1. The final sintering process in a Bi_2O_3 atmosphere makes it possible to have reasonably high bismuth concentrations. The bismuth is rather well homogeneously distributed in the bulk of the material. TEM observations show, however, a very thin, Bi-rich film on the grain boundaries. The results reported here refer to a sample with composition $0.78 \text{ ZrO}_2 - 0.206 \text{ YO}_{1.5} - 0.014 \text{ BiO}_{1.5}$.

The performance of the optical measurements were described elsewhere [ref.3].

Results

Yttria-stabilized zirconia doped with Bi_2O_3 (ZYB) is an efficient luminescent material at room temperature and below. Under uv excitation a bluish-white emission is observed.

In fig.1 we have given the 300 K emission spectrum for 300 nm excitation. This spectrum suggests that there is more than one emission band present. This is in fact the case as is shown in fig.2 where the 4.2 K measurements are given for suitable emission and excitation wavelengths. For the longer wavelength excitation we observe mainly the longer wavelength emission band. It is impossible to excite the shorter wavelength emission separately. However, by monitoring the shorter wavelength emission we find a shorter wavelength excitation maximum.

Since the host lattice absorption starts only at about 250 nm [ref.4], the luminescence spectra must be due to the Bi^{3+} ion. The centre with the longer wavelength emission will be designated by $\text{Bi}^{3+}(1)$, that with the shorter wavelength emission by $\text{Bi}^{3+}(s)$. The emission and excitation maxima of the luminescence of these centres are given in table I, together with some other relevant data.

Table I

Spectral data on the luminescence of ZYB and $\text{Y}_2\text{O}_3\text{-Bi}$

Sample	Luminescent centre	Emission maximum (nm)	Excitation maximum (nm)	Stokes shift (cm^{-1})
ZYB a)	$\text{Bi}^{3+}(s)$	400	305	7.800
	$\text{Bi}^{3+}(1)$	460	325	9.100
$\text{Y}_2\text{O}_3\text{-Bi}$ b)	$\text{Bi}^{3+}(C_2)$	520	340	10.000
	$\text{Bi}^{3+}(S_6)$	410	375	2.400

a) This work, values at 4.2 K; b) After ref.10.

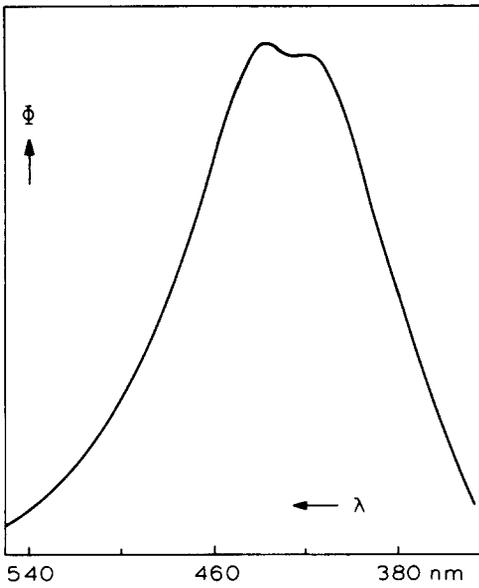


FIG. 1

Spectral energy distribution of the emission of ZYB at room temperature. Excitation is by 300 nm radiation. Φ denotes the spectral radiant power per constant wavelength interval in arbitrary units.

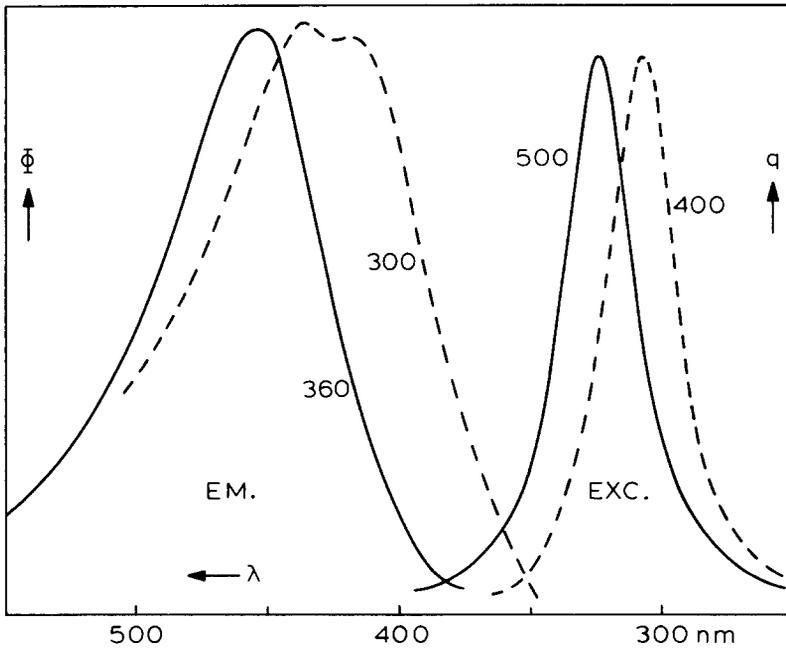


FIG. 2

Emission and excitation spectra of the luminescence of ZYB at 4.2 K. Right-hand side: excitation spectra; left-hand side: emission spectra. The numbers give the monitored emission wavelength and the excitation wavelength, respectively. For Φ , see fig. 1. q gives the relative quantum output in arbitrary units.

Discussion

The luminescence is due to the Bi^{3+} ions in ZYB. These have the $6s^2$ electron configuration. The excitation band corresponds to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ absorption transition. The emission at 4.2 K is due to the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition. At room temperature, however, the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition dominates [2]. The room temperature excitation maxima are at about 5 nm longer wavelength than those at 4.2 K, whereas the emission maxima are at the same position at both temperatures. This shows that the thermal shift of the ^3P states is just compensated by the $^3\text{P}_1 - ^3\text{P}_0$ energy difference. This difference is, therefore, estimated to be 500 cm^{-1} . This value is well in line with the value to be expected from the Stokes shift, viz. 400 cm^{-1} [ref.5].

The $^1\text{S}_0 \rightarrow ^1\text{P}_1$ transition is at about $10,000 \text{ cm}^{-1}$ higher energy than the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition, so that it is expected at about 250 nm in the case of ZYB. However, it is not observed in our excitation spectrum. The most probable explanation for this is the fact that the host lattice absorbs also at this wavelength and that energy transfer from the host lattice to the Bi^{3+} ions does not occur.

Fig.2 shows clearly that two different luminescent Bi^{3+} centres are present. Other Bi^{3+} centres are either not luminescent or have a much lower concentration. A careful comparison of fig.1 with the analogous part of fig.2 shows that at LHeT the spectrum is broader on the longer wavelength side. This may be due to such a Bi^{3+} centre (with low quenching temperature of the luminescence). Because this additional emission is weak and cannot be resolved spectrally, it will be neglected here. In view of the low activator concentration (1.4 %) and the very small spectral overlap between emission and excitation bands, the probability for energy transfer between the $\text{Bi}^{3+}(\text{s})$ and the $\text{Bi}^{3+}(\text{l})$ centres can be neglected. Because of this, the spectral data can be used to estimate the concentration ratio of these centres. Fig.1 shows that for relatively short wavelength excitation, which probably excites both centres equally, the emission of the $\text{Bi}^{3+}(\text{s})$ centre has about the same intensity as that of the $\text{Bi}^{3+}(\text{l})$ centre. Further, the excitation spectrum of 430 nm emission has a maximum in between the values of those for 400 and 500 nm emission. By monitoring 430 nm emission we observed about equal amounts of $\text{Bi}^{3+}(\text{s})$ and $\text{Bi}^{3+}(\text{l})$ emission. Obviously the excitation spectrum contains the excitation bands of both emissions with equal intensities. These results suggest that the concentrations of $\text{Bi}^{3+}(\text{s})$ and $\text{Bi}^{3+}(\text{l})$ in ZYB are about equal.

In ref.1 it was shown that the grain size in the sample investigated amounts to $3 \mu\text{m}$. The grain boundaries are strongly enriched with bismuth due to the formation of a liquid Bi_2O_3 -rich film around the grains during sintering. However, the major part of the bismuth is situated within the grains. In view of these results it cannot be excluded that one of the luminescent centres is situated in the bulk of the grains and the other in the grain boundaries. This seems improbable, however, in view of the derived concentration ratio. In addition, the Bi_2O_3 -rich layer is expected to show absorption at longer wavelengths than corresponds with the excitation bands and should not luminesce efficiently, certainly not at room temperature [6]. From this we conclude that both luminescent centres are situated in the bulk of the grains.

Let us now try to relate this to the defect chemistry of yttria-stabilized zirconia. Two yttrium ions are charge compensated by one oxygen vacancy. We assume that Bi^{3+} in ZYB replaces the Y^{3+} ions in a random way. That the presence of two

different cations (Zr^{4+} and Y^{3+}) on one and the same crystallographic sublattice would lead to the presence of two different Bi^{3+} centres is highly improbable. The cation distribution will only lead to a certain broadening of the emission band (inhomogeneous broadening). Therefore we have to relate the presence of more than one Bi^{3+} centre to the distribution of the oxygen vacancies.

In the case of complete association (i.e. two trivalent ions and one oxygen vacancy) it is impossible to imagine two Bi^{3+} centres in equal concentration. A model of association leading to association of one trivalent ion with an oxygen vacancy and the other trivalent ion without a nearest neighbour vacancy leads to two types of trivalent ions in equal concentration. However, a complete random distribution of the vacancies leads to a situation in which 64 % of the cations has no anion vacancies in the first coordination sphere, 30 % one vacancy and 6 % two vacancies (the vacancy concentration is 0.055, so that the probability for no vacancies in the first coordination sphere is $0.945^8 = 0.64$, and so on). This model leads to the presence of three different Bi^{3+} ions. However, the concentration of one of these is low (6 %) and the concentration ratio of the other two is not definitely excluded by our rather inaccurate estimation from the spectra. The experimental results suggest that the real situation is in between the random vacancy distribution and the partial association, with a tendency to be nearer to the latter.

A combination of investigations by Nowick et al. [7] have shown that in lanthanide (Ln)-doped CeO_2 half of the Ln^{3+} ions are associated with vacancies into charged pairs $(Ln_{Ce}^1 \cdot V_O^{2-})^*$ in the lower lanthanide concentration region. This conclusion is based on the random distribution of lanthanide ions (which at $T < 1000$ °C are frozen in) in combination with a rather complete association of a Ln^{3+} ion and one anion vacancy, the remaining Ln_{Ce}^1 being left unassociated. Dielectric and mechanical measurements support the existence of charged pairs in the concentrations required, whereas EPR measurements [8] indicate the existence of Ln^{3+} ions in cubic symmetry (LnO_8).

A similar situation seems to exist in the solid solutions under discussion, resulting in two types of Y^{3+} ions in equal concentration. If Bi^{3+} is randomly distributed over the two types of sites, two types of Bi^{3+} ions in equal concentration result. At higher concentrations this picture is obscured by the occurrence of clustering and domain formation [see e.g. ref.9]. This may give rise to additional types of sites.

In both models the $Bi^{3+}(s)$ centre is a BiO_8 group and the $Bi^{3+}(1)$ centre a BiO_7 group or the reverse.

Finally, it is interesting to compare the results on ZYB with those for Y_2O_3 - Bi^{3+} [ref.10]. Both are given in table I. The compound Y_2O_3 has a crystal structure which can be derived from fluorite by leaving 25 % of the anion sites vacant in an ordered arrangement. There are two cation sites, one with C_2 and the other with S_6 site symmetry. Both sites are coordinated by six anions and two vacancies. The latter lie along a face diagonal in the case of the C_2 site and along a body diagonal in the case of the S_6 site.

From table I we note that the luminescence characteristics of ZYB and Y_2O_3 -Bi are different as is to be expected from our model for ZYB. The value of the Stokes shift has been related to the degree of off-centre position of the Bi^{3+} ion [2]. In the small and centrosymmetrical S_6 site the Stokes shift is small as is to be expected. The Stokes shift increases in the sequence $Bi^{3+}(s)$ in ZYB $<$ $Bi^{3+}(1)$ in ZYB $<$

$\text{Bi}^{3+}(\text{C}_2)$ in Y_2O_3 . This suggests that the $\text{Bi}^{3+}(\text{s})$ centre is the centre without anion vacancies, i.e. the BiO_3 group. The weak additional emission at 4.2 K (see above) is situated in the same spectral region as the C_2 -site emission, so that this emission is perhaps due to Bi^{3+} with two vacancies on the nearest anion sites.

In conclusion the technique described in ref.1 is also suitable to prepare Bi^{3+} -activated phosphors when the host lattice has to be fired at high temperatures. In the case of ZYB the luminescence of the Bi^{3+} ion reveals structural details in spite of the broad-band character of the spectral transitions.

References

1. A.J.A. Winnubst and A.J. Burggraaf, *Mater. Res. Bull.*, in press
2. G. Blasse, *Rev. Inorg. Chem.*, in press;
C.W.M. Timmermans and G. Blasse, *J. Solid State Chem.*, in press;
A. Wolfert, E.W.J.L. Oomen and G. Blasse, *J. Luminescence*, to be published
3. H. Ronde and G. Blasse, *J. Inorg. Nucl. Chem.* 40, 215 (1978)
4. A.J.H. Macke, *J. Solid State Chem.* 18, 337 (1976);
A.J.H. Macke, thesis, Utrecht, 1976
5. G. Blasse and A.C. van der Steen, *Solid State Comm.* 31, 993 (1979)
6. R.K. Datta, *J. Electrochem. Soc.* 114, 1137 (1967)
7. A.S. Nowick, in: A.S. Nowick and G. Mirch (Eds.), "Diffusion in Solids",
Chapter "Atom transport in oxides of the fluorite structure", in press
8. M.M. Abraham, R.A. Weeks, G.W. Clark, and C.B. Finch, *Phys. Rev.* 137, A 138 (1965) and 148, 350 (1966)
9. R.J. Tesch, C.D. Wirkus and M.F. Berard, *J. Am. Ceram. Soc.* 65, 511 (1982)
10. G. Boulon, *J. Physique* 32, 333 (1971)