THE LUMINESCENCE OF YTTRIA STABILIZED ZIRCONIA DOPED WITH Bi₂O₃

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ABSTRACT

Yttria stabilized zirconia doped with Bi₂O₃ shows an efficient luminescence due to the Bi³⁺ ions. Two luminescent centres were observed which are ascribed to BiO₈ and BiO₇ groups.

Introduction

Recently Winnubst and Burggraaf [1] described a preparation method of monophasic yttria-stabilized zirconia doped with Bi₂O₃ (ZrO₂-Y₂O₃-Bi₂O₃). 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 Bi³⁺ ion in oxides [ref.2] we investigated also samples of yttria-stabilized zirconia doped with Bi₂O₃. Results are reported in this paper. We have found that the Bi³⁺ 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.

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Samples were prepared as described in ref.1. The final sintering process in a Bi₂O₃ 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 ZrO₂ - 0.206 YO₁.₅ - 0.014 BiO₁.₅.

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

Results

Yttria-stabilized zirconia doped with Bi₂O₃ (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 Bi³⁺ ion. The centre with the longer wavelength emission will be designated by Bi³⁺(1), that with the shorter wavelength emission by Bi³⁺(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 Y₂O₃-Bi

<table>
<thead>
<tr>
<th>Sample</th>
<th>Luminescent centre</th>
<th>Emission maximum (nm)</th>
<th>Excitation maximum (nm)</th>
<th>Stokes shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZYB a)</td>
<td>Bi³⁺(s)</td>
<td>400</td>
<td>305</td>
<td>7.800</td>
</tr>
<tr>
<td></td>
<td>Bi³⁺(1)</td>
<td>460</td>
<td>325</td>
<td>9.100</td>
</tr>
<tr>
<td></td>
<td>Bi³⁺(C₂)</td>
<td>520</td>
<td>340</td>
<td>10.000</td>
</tr>
<tr>
<td>Y₂O₃-Bi b)</td>
<td>Bi³⁺(S₆)</td>
<td>410</td>
<td>375</td>
<td>2.400</td>
</tr>
</tbody>
</table>

a) This work, values at 4.2 K; b) After ref.10.
FIG. 1
Spectral energy distribution of the emission of ZIB at room temperature. Excitation is by 300 nm radiation. \( \Phi \) denotes the spectral radiant power per constant wavelength interval in arbitrary units.

FIG. 2
Emission and excitation spectra of the luminescence of ZIB 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 \( \Phi \), 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 $^1S_0 \rightarrow ^3P_1$ absorption transition. The emission at 4.2 K is due to the $^3P_0 \rightarrow ^1S_0$ transition. At room temperature, however, the $^3P_1 \rightarrow ^1S_0$ 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 $^3P_1 - ^3P_0$ 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 $^1S_0 \rightarrow ^1P_1$ transition is at about 10,000 cm$^{-1}$ higher energy than the $^1S_0 \rightarrow ^3P_1$ 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 Bi$^{3+}$(s) and the Bi$^{3+}$(1) 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 Bi$^{3+}$(s) centre has about the same intensity as that of the Bi$^{3+}$(1) 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 Bi$^{3+}$(s) and Bi$^{3+}$(1) emission. Obviously the excitation spectrum contains the excitation bands of both emissions with equal intensities. These results suggest that the concentrations of Bi$^{3+}$(s) and Bi$^{3+}$(1) in ZYB are about equal.

In ref. 1 it was shown that the grain size in the sample investigated amounts to 3 $\mu$m. The grain boundaries are strongly enriched with bismuth due to the formation of a liquid Bi$_2$O$_3$-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$_2$O$_3$-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 (In$^{3+}$)-doped CeO$_2$ half of the Ln$^{3+}$ ions are associated with vacancies into charged pairs (In$^{3+}$,V$^{6+}$)$^*$ 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$^{3+}$ 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$_2$O$_3$-Bi$^{3+}$ [ref.10]. Both are given in table I. The compound Y$_2$O$_3$ 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$_2$O$_3$-Bi$^{3+}$ 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 <
Bi$^{3+}(C_2)$ in Y$_2$O$_3$. This suggests that the Bi$^{3+}(s)$ centre is the centre without anion vacancies, i.e. the BiO$_8$ 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.

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