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Crystal Structure and Luminescence of Compounds $A_3BC_{10}O_{20}$

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In this paper we describe compounds $A_3BC_{10}O_{20}$ (A = Sr, Ba, Pb; B = Ti, Ge, Sn; and C = Al, Ga). The crystal structure of $Ba_3TiAl_{10}O_{20}$ has been determined by neutron powder profile refinement. The luminescence of these compounds has been investigated. Apart from the titanate luminescence of $Ba_3TiAl_{10}O_{20}$, these compounds show a semiconductor type of luminescence.

1. Introduction

Investigations of quarternary compounds in the system $BaO-Fe_2O_3-SnO_2$ (*1*) led to the compound $Ba_3SnFe_{10}O_{20}$ with lattice parameters comparable to $Ba_3TiAl_{10}O_{20}$ (*2*) and $Pb_3GeAl_{10}O_{20}$ (*3*). We prepared several related compounds and determined the crystal structure of $Pb_3GeGa_{10}O_{20}$ by X-ray single-crystal methods (*4*). Single crystals of the other compounds were not available, so we decided to use the neutron powder profile refinement technique (*5*) in order to obtain precise structural information for $Ba_3TiAl_{10}O_{20}$.

Since similar compounds $A_3SiAl_{10}O_{20}$ (A = Sr, Ba) were successfully used as host lattice for luminescent materials (*6*), we also investigated the luminescence properties of some of the present compounds.

2. Experimental

We prepared the compounds by firing appropriate mixtures of $BaCO_3$, $SrCO_3$, GeO_2, TiO_2, SnO_2, Al_2O_3, and Ga_2O_3 in alumina crucibles at 1540 K for 2 weeks with repeated grinding. The lead compounds were prepared from the oxides at 1070 K. The neutron diffraction data were collected at 300 K on the powder diffractometer at the Petten High-Flux Reactor as described by van Laar *et al.* (*7*). A wavelength of 2.5903(3) Å was used and the complete range of data obtained ($5.4° < 2\theta < 155°$) was used in the refinement. Absorption and extinction effects were small and no corrections were made. For the trial model with space group $I2/m$ we used the atomic parameters of $Pb_3GeGa_{10}O_{20}$ (*4*). The variables in the refinement were:

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A scale factor, three half-width parameters defining the Gaussian lineshape, the counter zero-error, the unit-cell parameters, the atomic positional parameters, four isotropic temperature parameters, and an asymmetric parameter. The coherent scattering lengths assumed were: Ba—5.2, Ti—−3.4, Al—3.5, O—5.8 fm (*8*). Ti and Al were assumed statistically distributed over the octahedral positions (Ti, Al). The R factors are $R_{\text{nuclear}} = 2.88$ and $R_{\text{profile}} = 4.81$ (for a definition see Ref. (*5*)). A refinement with Ti statistically distributed over all octahedral and tetrahedral positions did not yield reliable results. A list of observed and calculated intensities is available from D. J. W. IJdo.

The performance of the optical measurements has been described previously (*9*).

3. Results

The compounds prepared are listed in Table I, together with their lattice parameters. The atomic parameters of $Ba_3TiAl_{10}O_{20}$ are given in Table II. The interatomic distances are presented in Table III.

TABLE I

LATTICE PARAMETERS OF COMPOUNDS INVESTIGATED

Compound	a (Å)	b (Å)	c (Å)	β (°)
$Sr_3GeAl_{10}O_{20}$	14.420(4)	11.242(3)	4.918(2)	90.72(1)
$Sr_3SnAl_{10}O_{20}$	14.533(3)	11.352(3)	4.967(1)	90.22(1)
$Sr_3GeGa_{10}O_{20}$	14.669(3)	11.603(2)	5.074(1)	90.91(1)
$Sr_3TiGa_{10}O_{20}$	14.684(5)	11.643(4)	5.081(2)	90.55(2)
$Sr_3SnGa_{10}O_{20}$	14.712(4)	11.698(4)	5.130(2)	90.47(1)
$Ba_3TiAl_{10}O_{20}$	14.888(1)	11.363(1)	4.978(1)	90.82(1)
$Ba_3GeFe_{10}O_{20}$	15.318(8)	11.783(6)	5.191(3)	91.40(2)
$Ba_3TiFe_{10}O_{20}$	15.327(7)	11.800(5)	5.172(2)	91.24(2)
$Ba_3SnFe_{10}O_{20}$[a]	15.359(4)	11.875(3)	5.227(2)	91.14(1)
$Ba_3SnIn_2Fe_8O_{20}$	15.439(11)	11.975(8)	5.292(4)	90.29(2)
$Ba_3SiGa_{10}O_{20}$	15.065(7)	11.611(6)	5.100(3)	91.09(2)
$Ba_3GeGa_{10}O_{20}$	15.115(6)	11.650(4)	5.099(2)	91.12(1)
$Ba_3TiGa_{10}O_{20}$	15.140(6)	11.705(3)	5.117(1)	91.00(1)
$Ba_3SnGa_{10}O_{20}$	15.177(4)	11.762(3)	5.156(1)	90.96(1)
$Pb_3GeGa_{10}O_{20}$	14.755(3)	11.705(2)	5.107(1)	90.39(1)

[a] Ref. (*1*).

TABLE II

ATOMIC PARAMETERS OF $Ba_3TiAl_{10}O_{20}$

	x	y	z	B (Å^2)
Ba(1)	0	0	0	0.12(.25)
Ba(2)	0.2773(5)	0	0.0320(13)	1.61(.20)
(Ti,Al)	0	0.5	0	0.54(.08)
(Ti,Al)	0	0.6368(26)	0.5	0.54(.08)
Al(3)	0.3529(4)	0.3607(6)	0.0116(11)	0.54(.08)
Al(4)	0.1375(5)	0.2906(6)	0.9768(13)	0.54(.08)
O(1)	0.4372(5)	0	0.8232(10)	0.07(.04)
O(2)	0.8952(4)	0	0.4190(11)	0.07(.04)
O(3)	0.2381(3)	0.3561(3)	0.9359(7)	0.07(.04)
O(4)	0.4139(3)	0.2441(4)	0.8487(8)	0.07(.04)
O(5)	0.8608(3)	0.1517(3)	0.8658(8)	0.07(.04)
O(6)	0.9309(3)	0.3801(3)	0.8216(7)	0.07(.04)

Table IV surveys the luminescence of these compounds at room temperature and at liquid nitrogen temperature and under short-wavelength and long-wavelength ultraviolet excitation. The luminescence of the three most efficient compositions has been studied in more detail.

The compound $Ba_3TiAl_{10}O_{20}$ shows one emission band with a maximum at about 500 nm, independent of the excitation wavelength. There is also one excitation band peaking at about 280 nm. The Stokes shift is about 2 eV. The thermal quenching temperature of the luminescence is at 300 K.

The compound $Ba_3GeGa_{10}O_{20}$ shows two emission bands peaking at 400 and 460 nm. There is one excitation band at about 250 nm. Their luminescence is quenched at room temperature.

The compound $Ba_3SnGa_{10}O_{20}$ shows similar characteristics, but the maxima are at longer wavelength. The emission bands peak at 500 and 570 nm, the excitation band at 290 nm. The quenching temperature is 340 K.

4. Discussion

4.1. Crystal Structure

The results of the structure refinement of $Ba_3TiAl_{10}O_{20}$ agree very well with those of

TABLE III

INTERATOMIC DISTANCES (Å) FOR $Ba_3TiAl_{10}O_{20}$

Ba(1)–O(2)	2.622(6)	2×
–O(5)	2.770(4)	4×
Ba(2)–O(1)	2.611(9)	
–O(5)	2.736(7)	2×
–O(3)	2.852(6)	2×
–O(6)	3.012(8)	2×
–O(3)	3.124(7)	2×
(Ti, Al)(1)–O(1)	1.872(5)	2×
–O(6)	1.918(4)	4×
(Ti, Al)(2)–O(1)	2.010(23)	2×
–O(4)	1.916(19)	2×
–O(6)	1.915(5)	2×
Al(3)–O(2)	1.767(7)	
–O(3)	1.747(7)	
–O(4)	1.805(7)	
–O(5)	1.771(4)	
Al(4)–O(3)	1.687(9)	
–O(4)	1.825(8)	
–O(5)	1.762(8)	
–O(6)	1.763(8)	

$Pb_3GeAl_{10}O_{20}$ (*3*) and $Pb_3GeGa_{10}O_{20}$ (*4*), except for some details in the coordination of Ba(2). The structure has been described by Vinek *et al.* (*3*), but is more completely described as follows. There are rings of six corner-sharing tetrahedra which have their apices in one direction. The rings form strings parallel to the *c* axis. The apices coincide with the apices of two other strings, in which the apices point to the opposite direction. In this way a ribbed plane is obtained; the twofold axes generate the other planes. Between the planes where the rings of tetrahedra are close together, Ba(1) is in octahedral coordination. Where the rings are far away from each other, channels are present which are occupied by Ba(2) in monocapped tetragonal, prismatic coordination and (Ti, Al) in octahedra sharing edges. Further, we find in the channels an oxygen not bound in the tetrahedral framework (O(1)). The coordination of Ba(2) is much more regular than that of Pb(2) in the compounds mentioned above. The asymmetric coordination of Pb(2) in the lead compounds can be ascribed to the presence of the $6s^2$ lone pair.

All compounds mentioned in Table I are isomorphous.

4.2. *Luminescence*

Let us first consider $Ba_3TiAl_{10}O_{20}$. From the constituents only the Ti–oxygen polyhedron is able to absorb ultraviolet radiation. This group is known to luminesce in a large number of host lattices (*10, 11*). The optical transitions involved are of the charge-transfer type. Since the tetrahedral titanate group absorbs only at wavelengths shorter than 250 nm (*11*), the 280-nm absorption must be due to an octahedral titanate group. This agrees with the results of the structure determination. The value of the Stokes shift is well in line with data observed for the titanate group in other host lattices (*11*). It has also been shown that the quenching temperature of this luminescence is determined by the position of the absorption edge (*12*). This relation makes for an excitation maximum at 280 nm, a quenching temperature around room temperature—in excellent agreement with the experimental results. The luminescence of $Ba_3TiAl_{10}O_{20}$ is, therefore, easy to interpret as being due to the octahedral titanate group.

The luminescence of the other compounds, however, is not so easy to as-

TABLE IV

LUMINESCENCE OF COMPOUNDS INVESTIGATED

	254-nm excitation		365-nm excitation	
	Room temperature	LNT	Room temperature	LNT
$Sr_3GeGa_{10}O_{20}$	—	blue	—	—
$Ba_3GeGa_{10}O_{20}$	—	blue	—	—
$Pb_3GeGa_{10}O_{20}$	—	yellow	—	orange
$Ba_3TiAl_{10}O_{20}$	weak yellow	yellow	—	—
$Sr_3SnGa_{10}O_{20}$	—	—	—	—
$Ba_3SnGa_{10}O_{20}$	weak orange	orange	weak orange	orange

sign. The ultraviolet absorption of $Ba_3GeGa_{10}O_{20}$ and $Ba_3SnGa_{10}O_{20}$ is due to the presence of ions with d^{10} configuration (Ge^{4+}, Sn^{4+}, Ga^{3+}). It has been shown that oxides of these ions usually luminesce, but that the emission transitions are due not to characteristic centers, but to levels within the forbidden gap (*13*). Only one compound has been studied in full detail, viz., β-Ga_2O_3 (*14, 15*).

The resemblance between the luminescence of β-Ga_2O_3 and that of $Ba_3GeGa_{10}O_{20}$ is striking. The former shows one excitation band at 4.8 eV with an ultraviolet emission at 3.1 eV and a blue emission at 2.6 eV. For the latter these values are 5.0, 3.1, and 2.7 eV, respectively. The crystal structure of β-Ga_2O_3 consists of GaO_4 and GaO_6 octahedra which are coupled together. This also resembles the situation for $Ba_3GeGa_{10}O_{20}$. For this reason the luminescence transitions are assigned in the same way as in β-Ga_2O_3, viz., the absorption edge is due to the lowest interband transition, the ultraviolet emission is due to the recombination of an electron with a self-trapped hole and the blue emission is due to the recombination of an electron on an oxygen vacancy or a gallium interstitial with a hole trapped on a gallium vacancy. The Ge^{4+} ion (isoelectronic with the Ga^{3+} ion) obviously does not disturb the band structure of the gallate subsystem. Without further experiments on single crystals (cf. Ref. (*14*)), a more detailed analysis cannot be given.

The luminescence of $Sr_3GeGa_{10}O_{20}$ is similar, as is to be expected. However, if ions are introduced with lower-lying levels, the optical transitions shift to lower energy. This is most clearly demonstrated by $Ba_3SnGa_{10}O_{20}$, which shows the same transitions as $Ba_3GeGa_{10}O_{20}$, but at some 0.5-eV-lower energy value. The Sn^{4+} ion must be responsible for this shift. Note that the absorption edge of SnO_2 is at lower energy than that of β-Ga_2O_3 or GeO_2. Probably the emission transitions occur in the neighborhood of the tin ion. It is not clear why $Sr_3SnGa_{10}O_{20}$ does not luminesce. It seems probable that an unknown impurity acts as a killer center. In $Pb_3GeGa_{10}O_{20}$ the presence of the Pb^{2+} ions must be responsible for the low-energy position of the emission, but the nature of the transition cannot be given with certainty.

Konijnendijk *et al.* (*6*) have indexed these and similar compounds orthorhombically, which seems to be incorrect in view of the present data. From a study of the luminescence of the system $Sr_{3-x}Ce_xSi_{1-x}Al_{10+x}O_{20}$ they conclude that the Ce^{3+} luminescence arises from only one type of center and that, therefore, all Sr^{2+} ions are at crystallographically identical positions. This cannot be correct. In view of the present analysis the Ce^{3+} ions have a preference for one of the two Ba sites (see Table II). Since the Ce^{3+} ion is smaller than the Sr^{2+} and Ba^{2+} ions, it seems obvious to assume that the Ce^{3+} ions occupy the octahedral Ba(1) sites.

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