980 *Inorg. Chem.* **1980**, *19*, 980-983

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Nitrite Complexes of Silver(I) in Molten Alkali Nitrates

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Received July 23, 1979

Potentiometric measurements with silver(I) concentration cells in melts of 1:1 (K,Na)NO_3 containing $AgNO_3$ and $NaNO_2$ have been performed in the temperature range 523–623 K. It is demonstrated that NO_2^- acts as a fairly weak ligand for Ag(I). Complexes with the formal compositions $AgNO_2$ and $Ag(NO_2)_2^-$ are detected, and their stability constants are determined. The disproportionation reaction $2AgNO_2 \rightarrow Ag^+ + Ag(NO_2)_2^-$ is favored by increased temperature. From estimated standard enthalpy and entropy changes, it is suggested that the addition of a second NO_2^- to Ag(I) according to $AgNO_2 + NO_2^- \rightarrow Ag(NO_2)_2^-$ occurs with a considerable structural rearrangement of solvent NO_3^- ions adjacent to silver. Application of the quasi-lattice formalism to the data gives temperature-dependent specific interaction parameters ΔA_1 and ΔA_2. $(\partial(-\Delta A_1)/\partial T)_{Z=5}$ can possibly be looked upon as a change in internal entropy, whereas it is highly doubtful if the basic assumptions of the theory hold for the second step.

Introduction

From aqueous and solid-state chemistry, the nitrite ion is known to act as an ambidentate ligand, being capable of coordinating both via oxygens to give nitrito complexes and via the nitrogen lone pair, giving nitro complexes. Although hard or soft character of the metal atom would to some extent enhance the tendency to O- or N-coordination, respectively, it seems that steric factors are most important in determining the coordination mode, at least in the solid state.[1]

The important role of the nitrite ion in the fundamental chemistry of molten alkali-metal nitrates has been elucidated in a number of studies on oxygen ion equilibria. This field of chemistry has been surveyed in a recent review by Kerridge.[2] So far, however, the ability of NO_2^- to complex metal ions in molten salts has received little attention.[3]

Boxall and Johnson[4] observed considerable shifts in the emf of silver(I) concentration cells as the solvent, molten $NaNO_3$, in one half-cell was gradually replaced by $NaNO_2$ at 309 °C. These shifts can be taken as an indication of a tendency of Ag(I) to complex with NO_2^- in the molten nitrate medium. We report results from a potentiometric study of the Ag^+–NO_2^- association in dilute solutions in the "standard" solvent melt 1:1 (K,Na)NO_3. The temperature and composition ranges accessible are limited by a number of potentially interfering reactions, such as the thermal decomposition of solvent NO_3^- to NO_2^-, the thermal decomposition of $AgNO_2$, and the oxidation of NO_2^- to NO_3^- by air oxygen. These interferences will be discussed in a later section, but it should be noted here that the thermal decomposition of $AgNO_2$ makes the solubility technique, which has been successfully used in aqueous solutions,[5-7] inapplicable as a complement to the potentiometric measurements.

Experimental Section

Chemicals from Merck A. G., p.a. grade, were used without further purifications. The (K,Na)NO_3 solvent was prepared and dried as described previously.[8] Nitrite was added as $NaNO_2$ only, since KNO_2 appeared to be difficult to handle in the anhydrous state. In this way the K:Na balance was at most shifted from 1:1 to 1:1.04 in the melt, which was considered to have a negligible influence on the complex stabilities under study. $NaNO_2$ was dried at 120 °C for at least 24 h and stored over P_2O_5 prior to use.

Table I. Review of Experimental Material[a]

T, K	n	10^4C_0, mol kg^{-1}	$(C_{NO_2^-})_{max}$, mol kg^{-1}
523	18	3.3	0.20
538	33	3.5	0.16
553	18	3.7	0.17
588	19	4.2	0.09
623	15	4.6	0.09

[a] $C_{Ag} \approx 1 \times 10^{-3}$ mol kg^{-1} in all melts. n = number of melt compositions studied at a given temperature. C_0 and $(C_{NO_2^-})_{max}$ are initial and final total concentrations of nitrite.

The emf was measured for concentration cells

$$\mathrm{Ag}\left|\begin{array}{l} C_{NO_2^-}\ NaNO_2 \\ C_{Ag}\ AgNO_3 \\ (K,Na)NO_3 \end{array}\right|\ \left|\begin{array}{l} C^\circ{}_{Ag}\ AgNO_3 \\ \\ (K,Na)NO_3 \end{array}\right|\mathrm{Ag}$$

Here $C_{NO_2^-}$ and C_{Ag} are total concentrations of nitrite and Ag(I), respectively, in the test melt, and $C^\circ{}_{Ag}$ correspondingly defines the total Ag(I) concentration in the reference half-cell. The melts were kept in Pyrex glass vessels in an aluminum-block precision thermostat, fitted with a proportional-temperature regulator, type CR/DHS/PID/SCR from Eurotherm, Worthing, England. Details of the furnace equipment, cell construction, and electrodes can be found in previous papers.[8,9] In this work, however, the asbestos fiber junction between the half-cells was replaced by a ceramic plug (5 mm × 1 mm in diameter) supplied by Radiometer, Copenhagen. The long-time performance of the reference half-cells was considerably improved by this replacement.

The cell was usually set up with $C_{Ag} = 1 \times 10^{-3}$ mol kg^{-1} and $C^\circ{}_{Ag} = 3 \times 10^{-3}$ mol kg^{-1}. The test melt was left with vigorous stirring for about 18 h before any addition of nitrite was made. In this way an equilibrium concentration of NO_2^-, corresponding to the local partial pressure of oxygen in the laboratory air, was built up by thermal decomposition of NO_3^-.[10]

Successive additions of $NaNO_2$ to the test melt were then made, and the emf was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC data logging unit from Mess + System Technik, München. The E values were measured to ±0.05 mV. Stable readings were as a rule obtained within 10 min after each addition of $NaNO_2$.

All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range 250–350 °C. Maximum concentrations of nitrite at each temperature are given in Table I.

Results and Discussion

Some General Considerations. The thermal decomposition of the nitrate melt according to eq 1 produces an equilibrium

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$$NO_3^- \rightarrow NO_2^- + {}^1/_2O_2(g) \qquad (1)$$

"background" concentration, C_0, of NO_2^- at each temperature. From the data of Kust and Burke,[10] obtained in the range of 568–613 K, we have estimated C_0 after correction to our laboratory air pressure of O_2, 0.2 atm, assuming constant $\Delta H°$ and $\Delta S°$ for process 1 in the range 523–623 K. The total concentration of nitrite, $C_{NO_2^-}$, is then calculated as $C_{NO_2^-} = C_0 + C'$ in every melt under study. Here C' is a nominal quantity, computed from the added amount of $NaNO_2$. The estimated C_0 values are actually negligible (Table I), and they may be impaired by substantial errors without violating our determination of the compositions and stabilities of the Ag(I) complexes.

In melts having a high concentration of NO_2^-, $C_{NO_2^-}$ can decrease with time due to two different processes. First, the reversal of (1) occurs as shown in eq 2. Second, in the absence

$$NO_2^- + {}^1/_2O_2(g) \rightarrow NO_3^- \qquad (2)$$

of solid $AgNO_2$ a reaction which can be described conveniently by eq 3[11] may take place.

$$Ag^+ + NO_2^- \rightarrow Ag(s) + NO_2(g) \qquad (3)$$

The kinetics of reaction 2 in 1:1 $(K,Na)NO_3$ has been thoroughly studied by Paniccia and Zambonin.[12] It may be inferred from their rate constants that the maximum average oxidation rate amounts to about 1×10^{-5} mol kg^{-1} h^{-1} in the most NO_2^--rich melts ($C_{NO_2^-} = 0.1$ mol kg^{-1}) at 623 K, so this process has no practical influence on the potentiometric measurements. Hence, the upper practical concentration limit for NO_2^- (and Ag^+) is set by reaction 3. This process could be followed experimentally as a drift in the emf when the product $[Ag^+][NO_2^-]$ becomes large. Consequently the maximum NO_2^- concentration that was used in the computations of stability constants, $(C_{NO_2^-})_{max}$ in Table I, was determined by the requirement that stable emf readings should be recorded for at least 30 min.

Table I reviews the experimental material.

Treatment of Experimental Data. Liquid-junction potentials are negligible within the range of NO_2^- concentrations used in this study.[4] The quantity $C_{Ag}/[Ag^+]$ can thus be calculated from the emf of the cell as

$$\left(\frac{C_{Ag}}{[Ag^+]}\right)_c = \exp\left[\frac{F}{RT}(E_0 - E_c)\right] \qquad (4)$$

Here the index c denotes quantities pertaining to systems with $C_{NO_2^-} = c$ and E_0 refers to $C_{NO_2^-} = 0$. Experimental values of E_0 are, however, not strictly available due to the thermal decomposition of NO_3^-. The values used in the calculations are actually measured for $C_{NO_2^-} = C_0$. By use of the stability constants, determined with these approximate E_0 and eq 5, the errors introduced in $(E_0 - E_c)$ with this approximation can be estimated to ≤0.02 mV, which is less than the accuracy in the measured emf. Therefore, no correction of E_0 to adjust for process 1 has to be made.

In a set of preliminary experiments at 280 °C it was ascertained that $C_{Ag}/[Ag^+]$ was independent of C_{Ag} within the concentration range accessible. All data were hence treated according to eq 5 with the assumption of mononuclear species

$$C_{Ag}/[Ag^+] = \sum_{i=0}^{N} \beta_i [NO_2^-]^i \qquad \beta_0 = 1 \qquad (5)$$

only. In eq 5

$$\beta_i = [Ag(NO_2)_i^{1-i}][Ag^+]^{-1}[NO_2^-]^{-i} \qquad (6)$$

is the overall stability constant for $Ag(NO_2)_i^{1-i}$ according the simplified equilibrium model

$$Ag^+ + iNO_2^- \rightleftarrows Ag(NO_2)_i^{1-i} \qquad (7)$$

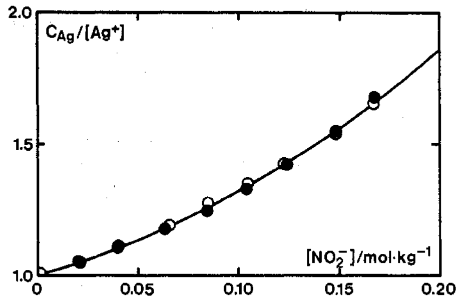

Figure 1. $C_{Ag}/[Ag^+]$ vs. $[NO_2^-]$ in molten 1:1 $(K,Na)NO_3$ at 553 K. Filled and unfilled symbols represent duplicate runs.

Table II. Overall Stability Constants β_i for Ag^+–NO_2^- Complexes in Molten 1:1 $(K,Na)NO_3$[a]

T, K	β_0	β_1, mol^{-1} kg	β_2, mol^{-2} kg^2
523	1.00 ± 0.02	2.9 ± 0.4	6 ± 2
538	1.00 ± 0.05	2.5 ± 0.5	7 ± 4
553	1.00 ± 0.01	2.1 ± 0.3	11 ± 1
588	1.00 ± 0.01	1.7 ± 0.5	18 ± 6
623	1.00 ± 0.02	1.2 ± 0.8	29 ± 8

[a] The limits of error represent 95% confidence limits.

Figure 1 displays experimental results from two duplicate series of measurements at 280 °C as an example of the spacing of data. The $C_{Ag}/[Ag^+]$ data at 280 °C and all other temperatures are well described by second-degree polynomials in $[NO_2^-]$, i.e., by complexes with the formal compositions $AgNO_2$ and $Ag(NO_2)_2^-$. Preliminary sets of β_i were obtained from regression analyses with the approximation $[NO_2^-] = C_{NO_2^-}$. Better values of $[NO_2^-]$ to be used in an interative process were obtained from eq 8, where the average ligand

$$[NO_2^-] = C_{NO_2^-} - \bar{n}C_{Ag} \qquad (8)$$

number $\bar{n}$ is calculated from the provisional constants. Only one cycle was necessary to obtain sufficient convergence in the parameter values. The results are given in Table II.

The data of Table II reveal that the general pattern from aqueous solution chemistry[7]—rather weak complexation stopping with $Ag(NO_2)_2^-$—is followed in nitrate melts as well. It is noteworthy, however, that $Ag(NO_2)_2^-$ becomes more important as the temperature is increased, indicating an entropy-favored second complexation step in nitrate melts. This can also be looked upon as a favorable disproportionation of the 1:1 species

$$2AgNO_2 \rightleftarrows Ag^+ + Ag(NO_2)_2^- \qquad (9)$$

due to an entropy gain. The overall complexation of silver is, however, fairly constant as the temperature is changed. This is clear from Figure 2, showing the fraction α of silver present as Ag^+, $AgNO_2$, and $Ag(NO_2)_2^-$ as a function of $[NO_2^-]$ at 523 and 623 K. At $[NO_2^-] = 0.1$ mol kg^{-1} about 30% of Ag(I) is complexed by NO_2^- irrespective of the temperature, whereas $AgNO_2$ is the predominating complex at 523 K and $Ag(NO_2)_2^-$ dominates at 623 K.

Estimates of Thermodynamic Parameters. $\Delta H°_i$ and $\Delta S°_i$ (i = 1 and 2) for the two successive steps of complexation, schematically written as

$$Ag^+ + NO_2^- \rightarrow AgNO_2 \qquad (10)$$

$$AgNO_2 + NO_2^- \rightarrow Ag(NO_2)_2^- \qquad (11)$$

have been estimated from a study of $\Delta G°_i = RT \ln K_i$ as a

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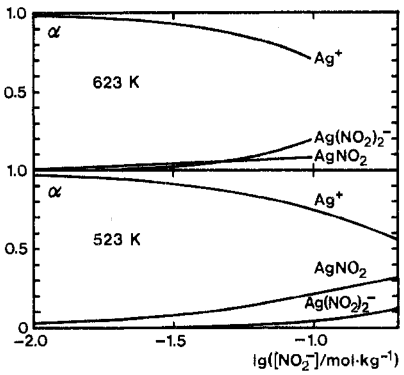

Figure 2. The fraction α of Ag(I) present in different species in 1:1 (K,Na)NO_3 at 523 and 623 K as a function of the nitrite concentration in the melts. The curves—calculated from the constants of Table II—are extended over the [NO_2^-] range experimentally covered at the two extreme temperatures.

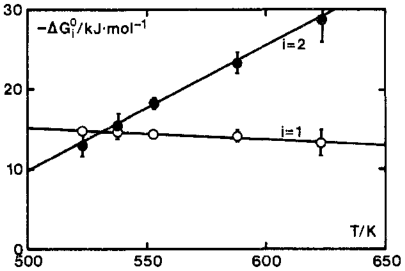

Figure 3. Plots of $-\Delta G^\circ_i$ for reactions 10 and 11 vs. T. The equations of the solid lines are defined by the parameters of Table III.

Table III. Estimated Standard Enthalpy and Entropy Changes for $Ag(NO_2)_{i-1}{}^{2-i} + NO_2^- \rightarrow Ag(NO_2)_i{}^{1-i}$ in 1:1 (K,Na)NO_3 Melts, 250–350 °C[a]

i	ΔH°_i, kJ mol^{-1}	ΔS°_i, J K^{-1} mol^{-1}
1	−23 ± 2	−15 ± 3
2	69 ± 9	157 ± 16

[a] Stated errors define 95% confidence limits.

function of T, K_i being the stepwise equilibrium constants for (10) and (11). The standard state chosen relates to unity ion fractions.

From Figure 3 it is seen that both ΔG°_1 and ΔG°_2 are good linear functions of T, so ΔH°_i and ΔS°_i have been estimated as constants by linear regression analysis. In doing so we have given every data point an individual weight proportional to $(\sigma_i(T))^{-2}$, where $\sigma_i(T)$ is given by eq 12 and 13. Here $\sigma(\beta_i)$

$$\sigma_1(T) = RT(\sigma(\beta_1)/\beta_1) \qquad (12)$$

$$\sigma_2(T) = RT\left\{\left[\frac{\sigma(\beta_1)}{\beta_1}\right]^2 + \left[\frac{\sigma(\beta_2)}{\beta_2}\right]^2\right\}^{1/2} \qquad (13)$$

is the estimated standard deviation in β_i at the temperature in question. Intervals corresponding to $2\sigma_i$ are marked around every point in Figure 3. The resulting parameters are given in Table III.

The first step of complexation is markedly exothermic, but the association is also disfavored by a considerable loss in entropy. This thermodynamic pattern is analogous to what has been found for aqueous solutions.[7] For the second step, however, no such similarity is found. The process is highy endothermic and is energetically favored by a remarkedly large gain in entropy in the molten nitrate medium. No definite explanation of this remarkable behavior can of course be given here, but a qualitative interpretation will be suggested.

The first step (eq 10) could be looked upon simply as a 1:1 exchange of NO_3^- for NO_2^- on an anionic quasi-lattice or alternatively an associative process involving a change in the silver nitrate interaction mode from bidentate to monodentate. The negative ΔS°_1 may—at least in part—be due to a change in internal degrees of freedom for the NO_2^- and NO_3^- involved, and the large exothermic ΔH°_1 may originate from a creation of a comparably strong Ag–N bond to NO_2^-. When the second ligand is to be added, structural demands of $Ag(NO_2)_2^-$, imposed by, e.g., a linear N–Ag–N geometry, would require a much larger number of silver nitrate oxygen bonds to be broken in step 11 (as compared to (10)), resulting in a positive ΔH°_2. Such a release of nitrate ions should also be associated with a predominantly configurational entropy gain.

A mechanistic description along these lines can qualitatively explain the thermodynamic difference between the two successive steps in melts as well as the contrast between the thermodynamics of the second step in water solution and nitrate melt. It should be remembered, however, that no clear-cut supporting structural evidence for preferential nitrogen coordination to Ag in solid compounds can be found. There are both O and N contacts with Ag in solid $AgNO_2$[13] as well as in the ferroelectric and paraelectric modifications of $AgNa(NO_2)_2$[14] and $Ag(NH_3)_2Ag(NO_2)_2$[15]—the two latter compounds with orientational NO_2^- disorder.

Application of Quasi-Lattice Formalism. The quasi-lattice theory for pair association in reciprocal ionic melts[16] has previously been applied to 1:1 complexation reactions between silver(I) and a number of divalent oxoanions in alkali nitrate melts by Sacchetto and co-workers.[17,18] They found a reasonably good agreement between model and experimental results in one-component solvents as well as mixed-cation solvents after modification of the model to account for temperature variations in the quasi-lattice association energy parameter ΔA_1 due to the presence of two different solvent cations.[19] Apparently, the anion charge inequality had no effect on the applicability of the model though structural rearrangements violating the basic assumptions of the theory are likely to occur when divalent ligand anions are mixed with NO_3^- ions.

In view of this our results clearly offer a good opportunity to test the applicability of the quasi-lattice model on association with a polyatomic ligand in a system of equally charged constituent ions. We calculated ΔA_1 and ΔA_2 for processes 10 and 11 by using the straightforward formalism of the generalized theory given by Blander.[20] The quasi-lattice coordination number Z was set equal to 5 in order to conform to the previous calculations by Sacchetto and co-workers.[17,18]

As might be expected from the magnitudes of ΔS°_1 and ΔS°_2, there is a considerable variation in ΔA_1 and ΔA_2 with temperature. The temperature dependence can be effectively rationalized as

$$\Delta A_i = a_i + b_i T \qquad (14)$$

with constant values of a_i and b_i for i = 1 and 2. These parameters were estimated by linear regression analysis using

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the same weighing scheme as described for the study of $\Delta G°_i$ vs. T. For a_i the following values are found: $a_1 = 19 \pm 2$ kJ mol^{-1}, $a_2 = 59 \pm 6$ kJ mol^{-1}. For b_i, we have $b_1 = 20 \pm 3$ J K^{-1} mol^{-1} and $b_2 = -133 \pm 12$ J K^{-1} mol^{-1}. The parameters, referring to the same standard state as $\Delta H°_i$ and $\Delta S°_i$, are given within 95% confidence limits.

Obviously, the positive value of b_1 cannot be explained by the presence of two different solvent cations, since the modified theory by Bombi and Sacchetto[19] predicts $(\partial(\Delta A_1)/\partial T)_Z \leq 0$. In the present case it seems more reasonable to adopt the view that $-b_1 = (\partial(-\Delta A_1)/\partial T)_{Z=5}$ largely expresses a change in internal entropy (ΔS_{int}) of the polyatomic ions exchanging on the anion sublattice of the melt. Actually $\Delta S_{\text{int}} = -20$ J K^{-1} mol^{-1} appears to be of a more reasonable order of magnitude than $\Delta S_{\text{int}} = 80$ J K^{-1} mol^{-1}, which can be calculated (with $Z = 5$) for Ag^+–CN^- association in 1:1 (K,Na)NO$_3$ melts by use of data given by Manning and Blander.[21] This comparison is made here, since the study of Manning and Blander constituted the only source of information on univalent polyatomic ligand behavior in nitrate melts prior to the present work. As for the second step of association (eq 11) the large negative value of b_2 seems to be inconsistent with both "mixed solvent" and "internal entropy" explanations. For reasons already mentioned in the discussion of $\Delta H°_2$ and $\Delta S°_2$ it may also be seriously questioned if the basic quasi-lattice assumptions do hold at the attachment of a second NO_2^- to $AgNO_2$. Finally it is to be stressed that too much emphasis should not be put on the absolute values of a_i and b_i since they are influenced by the choice of Z.

Concluding Remarks. The ability of nitrite ion to form metal complexes in nitrate melts as in aqueous solutions is clearly demonstrated. A definite conclusion about the coordination mode (nitro or nitrito) cannot be made, however, until more detailed information is available. The effects of size, charge, and chemical character of the central atom of the ligand on the thermodynamics of metal complexation with oxoanions in melts should be known. The previously cited works by Sacchetto and others[17,18] give some insight into these problems, and more information is hopefully to be gained from thermodynamic studies of a number of pertinent systems, which are in progress at our laboratory.

Acknowledgment. Experimental assistance by Miss Katrin Karlsson and Miss Kristina Andersson is gratefully acknowledged. This study has been supported by a grant from the Swedish Natural Science Research Council.

Registry No. Ag(NO$_2$)$_2^-$, 35772-22-6; AgNO$_2$, 7783-99-5; KNO$_3$, 7757-79-1; NaNO$_3$, 7631-99-4; AgNO$_3$, 7761-88-8; NaNO$_2$, 7632-00-0.

Supplementary Material Available: Table IV, giving experimental data C_{Ag}, $C_{NO_2^-}$, and $(E_0 - E_c)$ and calculated $C_{Ag}/[Ag^+]$ and $[NO_2^-]$ for all investigated melts (8 pages). Ordering information is given on any current masthead page.

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High-Pressure Synthesis, Characterization, and Properties of Europium(II) Metaborate and Europium(II)-Activated Strontium and Calcium Metaborates

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Received August 14, 1979

High-pressure syntheses and characterization by magnetic susceptibility and luminescence measurements were made on europium(II) metaborate (EuB_2O_4) and Eu^{2+}-activated alkaline earth metaborates (SrB_2O_4:Eu^{2+} and CaB_2O_4:Eu^{2+}). The pressure–temperature phase diagram of EuB_2O_4 was determined by X-ray analysis. This diagram consists of the following four regions: phases I, III, and IV and the decomposed phase $EuB_4O_7 + Eu_2B_2O_5$. Phase EuB_2O_4 (IV) was paramagnetic whereas other phases were antiferromagnetic. It was found that the high-pressure phases of EuB_2O_4, SrB_2O_4:Eu^{2+}, and CaB_2O_4:Eu^{2+} gave the band emissions based on a $4f^7$–$4f^65d$ transition and the peak positions of their emissions shifted to long wavelength with transformation into the high-pressure phases. The emissions of EuB_2O_4 consist of a weak band at about 370 nm for the phases I and III, a band at about 410 nm for the phase IV, and two bands at about 368 and 395 nm for the decomposed phase. Also their emission intensities drastically increased with changing from phase III to IV; particularly SrB_2O_4(IV):Eu^{2+} was found to be an efficient photoluminescent material. Compound $Sr_{0.99}Eu_{0.01}B_2O_4$ gives a strong emission at 395 nm, and its quantum efficiency (about 60%) under an optimum (313 nm) excitation was about 100 times higher than that of the phase I. These results were discussed by considering the relationship between their crystal structures and theories for the magnetic interaction and energy transfer phenomena.

Introduction

Divalent europium, Eu(II), compounds have been synthesized because of their magnetic and spectroscopic properties. The arrangement of outer electrons of the Eu^{2+} ion is a $4f^7$ configuration, as well as the Gd^{3+} ion,[1] and some of Eu(II) compounds have unique magnetic properties on account of the magnetic exchange interactions between neighboring Eu^{2+} ions.[2-4] In addition the Eu^{2+} ion gives a line or a band emission based on the $4f^7$–$4f^7$ or the $4f^7$–$4f^65d$ transition,[5] and several Eu^{2+}-containing phosphates[6] and halides[7] are very efficient photoluminescent materials. Among Eu^{2+}-activated

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