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Iron Luminescence Thermal Effects in Sodium β″-Alumina

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Powder $NaAl_5O_8$ doped with Fe^{3+} emits two broadbands at 705 and 758 nm. The shape of the combined emission depends on the annealing time of the samples and it is affected by the temperature of the samples, even below room temperature. It is concluded that these features are due to the occupation of at least two crystallographic inequivalent sites by the Fe ions in the sodium β″-aluminate: the BR sites (I) in the conduction region and Al(3) sites (II) of the spinel blocks near to the conduction plane. It is proposed that iron diffusion from I sites to vacant II sites should also occur in the temperature range below room temperature after the samples are submitted to long annealing times at synthesis temperature.

Introduction

Sodium β″-alumina is a superionic compound with a crystallographic rhombohedral structure belonging to the space group $R\bar{3}m$ and with the ideal formula $NaAl_5O_8$ (*1, 2*). The unit cell contains approximately six formula units consisting of spinel-like blocks (11.3 Å in thickness) spaced by column oxygens (cO) in Al–O–Al bindings; these Al(3) sites are tetrahedrally coordinated with C_{3v} symmetry (*3*). The gap between spinel blocks forms the Na conduction plane (*1*). The oxygen layers above and below the conduction plane are always staggered, and the Na^+ ions are inside tetrahedral Beevers-Ross (BR) sites formed by oxygens, 2.57 Å from the apex oxygen and 2.59 Å from the triangular base; about 17% of the BR sites are vacant (*1*).

The compound is nonstoichiometric ($Na_{(1+a)}Al_5O_8$ with $a > 0$), and its structural stability is due to the existence of defects (*4*). The powder binary phases reported in the literature (*2, 3, 5*) are soda-rich and the exact Na^+ content in these compounds is unknown (*3*). Long annealings above 1250°C reduce the Na/Al ratio from about 1/5 to about 1/7 (*6*). The binary compound has excess of positive charge due to sodium ions and the structure can be stabilized by doping with Mg^{2+} in order to grow large crystals (*3*). This stabilization is obtained because the Mg^{2+} ions substitute for Al^{3+} ions in AlO_4 sites near the center of the spinel blocks (Al(2) sites), and next to the conduction planes (Al(3) sites) (*7*). For the structure of the powder binary compound it has been proposed that only about 83% of the Al(3) sites are occupied by Al^{3+} ions (*2*). The excess of negative charge inside the spinel blocks, which is due to the Mg^{2+} exchange with Al^{3+} ions, compensates the positive charge excess due to Na. Since

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many powder binary phases have been obtained, and vacancies in Al(3) sites due to sodium excess was reported in sodium β-alumina (*8*), the role of Na loss and Al(3) vacancies in both the change compensation and the stabilization of the binary-phase powder compounds remains an open question.

The β''_{Na} alumina is an ultraviolet- to infrared-transparent host appropriate for the observation of the luminescence of impurity ions. For this material rare earth (RE) impurity emissions have been reported (*9*). In highly RE-substituted β''_{Na} (resulting from ion exchange of RE ions for the Na ions), the RE ions are located mainly in the BR and mid-oxygen (mO) sites; the mO sites are the interstitial sites between cO. It is known that RE ions cannot easily enter into oxygen spinel blocks, and RE doping by sintering procedures is very difficult and yields phase-mixed products (*9*). Transition metal (TM) impurity ions, however, can enter into oxygen spinel blocks, and do not cause phase separation. Studies on TM (Mn^{2+} and Cu^{2+}) in β''_{Na} were also reported showing that they occupy Al(3), BR, and mO sites (*10, 11*). For Mn^{2+}-doped β''_{Na}-alumina a Mn^{2+} migration to Al(3) sites is reported which increases with the annealing time (*10*).

Fe^{3+} ions emit a characteristic luminescence in tetrahedrally coordinated sites of binary oxide compounds with spinel-like structures (*12, 13*); and Fe-doped β_{Na}-alumina presents luminescence due to the iron ions (*14*). The iron ions do not have any site preference in oxide spinel hosts (*15*), and it should be expected that ready BR sites are the most probable ones. However, charge compensation should play a role in site distribution when Fe^{3+} doping is made by substituting Al^{3+} stoichiometrically. The possibility that impurity iron ions enter sites between spinel blocks, and that their luminescence could show effects due to ionic mobility motivated this work. This report presents results of an investigation on the thermal treatment effects (during and after the sample preparation) in the Fe^{3+} luminescence of the Fe^{3+}-doped β''_{Na}-alumina. Since the iron contents used are low ($\leq$0.5% at./mole), the samples could not be made by ion exchange and a sintering doping procedure was chosen.

Experimental Procedures

Powder compounds were prepared at temperatures between 1100 and 1200°C (*5*), with the β''_{Na}-alumina host having the binary oxide composition $Na_2O.5Al_2O_3$. The Fe^{3+} doping was achieved by Al^{3+} substitution according to the stoichiometry given by $NaAl_{5-x}Fe_xO_8$ and the nominal Fe^{3+} content (x) varying from 0.005 to 0.025. As in Refs. (*2*) and (*5*), MgO or Li_2O oxides were not added. The dry constituents $Al(OH)_3$, Na_2CO_3, and Fe_2O_3 were mixed, ground, and pressed, then heated in platinum boats, under an oxygen-rich atmosphere, in a Kanthal-type furnace with internal shield of high-purity recrystallized alumina. Two thermal treatments were adopted: (i) heating at 1100°C during 4 hr followed by another heating at 1200°C for 12 hr; (ii) two successive heat treatments at 1100°C of 4 hr each (*5*). In both procedures the samples were ground and pressed again after the first step and all cooling rates were 4°C/min. The presence of Fe^{3+} was verified in trial samples by Mössbauer measurements using ^{57}Fe-enriched Fe_2O_3. The Mössbauer spectra obtained show the presence of at least two inequivalent Fe^{3+} sites in this compound. All samples were also examined by X-ray diffraction to verify their β'' phase. Results from this structure analysis will be reported separately. The excitation and emission spectra presented in this report were obtained by procedures described elsewhere (*13*). Since Cr^{3+} is the most probable luminescent contaminant in these phosphors, trial samples with concentrations of less than 0.5% at./mole of this impu-

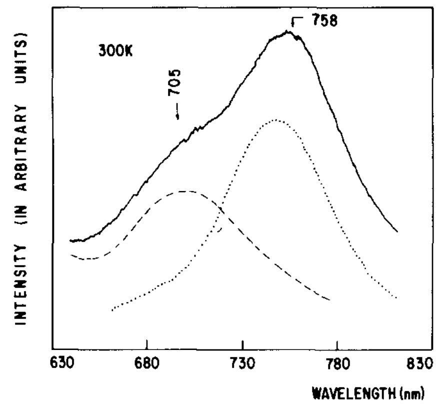

FIG. 1. The $NaAl_5O_8 : Fe^{3+}$ emission at room temperature for excitations at 395 nm (full line), 345 nm (dotted line), and 456 nm (dashed line).

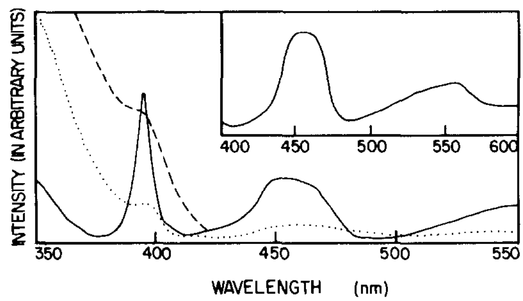

FIG. 2. The $NaAl_5O_8 : Fe^{3+}$ excitation at 77 K. The full line is the excitation of the 705-nm emission band; the insert of the figure shows the 450- and 550-nm excitation bands. The dotted line is the excitation of the 758-nm emission band and the dashed line is the same excitation at 300 K.

rity were prepared for comparison (*13*). These Cr^{3+} samples show a narrow luminescence band at 708 nm and two broad satellites at 693 and 701 nm. From these results it is concluded that the luminescence described in this work are due to Fe^{3+} impurities.

Results

Figure 1 shows the room-temperature red emission of the Fe^{3+}-doped β''_{Na}-alumina with a 0.025 iron concentration. The emission consists of two broadbands with barycenters at 705 and 758 nm. These bands can be selectively excited at 456 and at 345 nm, or simultaneously at 395 nm. The room-temperature decay times are 2.8 ms for the 705-nm band, and 1.7 ms for the 758-nm band.

Figure 2 shows the 77 K excitation spectra, obtained for the peak positions of the two emissions. Both excitation spectra have an intense ultraviolet (UV) band, which is partially shown in Fig. 2. For the 705-nm emission the UV excitation starts at 370 nm (at 77 K) and there are three bands at 395, 450, and 550 nm. The 450- and 550-nm bands (shown in the insert of Fig. 2) have structures which are typical of a low cubic symmetry site. Within the limit of our experimental sensitivity the 758-nm emission band is not excited at wavelengths above 440 nm. At 77 K its excitation consists of a UV band starting at about 410 nm. At room temperature this UV excitation has at 395 nm an intensity which is comparable to the narrow band of the excitation spectra of the 705-nm emission band, as shown by the dashed line of Fig. 2.

The main result of this work is the spectra shown in Fig. 3 for the room-tempera-

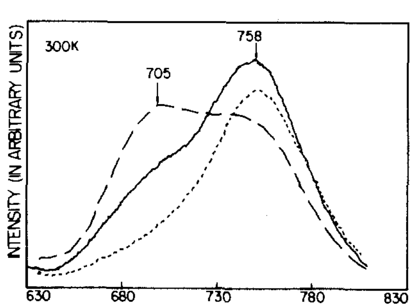

FIG. 3. Change in the shape of $NaAl_5O_8 : Fe^{3+}$ emission caused by thermal treatment. All spectra were obtained at room temperature exciting at 395 nm. ---, The emission of samples prepared with short annealing times. —, The emission of samples prepared with long annealing times. ---, The emission of samples also prepared with long annealing times after cooling to 5 K.

ture emission bands excited at 395 nm. As it can be seen in this figure the spectral shape can be modified by heat treatment of the samples. The main features observed are: (i) samples prepared with short annealing times present the smallest relative intensity of the 705-nm band (short dashes of Fig. 3); (ii) there is an increase of the relative intensity of the 705-nm band for those samples submitted to long annealing times (solid line of Fig. 3); (iii) the relative intensity of the 705-nm emission is enhanced after cooling below room temperature (long dashes of Fig. 3). This enhancement occurs only with those samples which were previously submitted to annealing times of about 10 hr at 1200°C.

Analysis

The excitation spectra associated with the 705-nm emission can be assigned to crystal-field transitions of high-spin Fe^{3+} ion in an approximately cubic (tetrahedral) site of the spinel block. Since the two emission bands shown in Figs. 1 and 3 both have different excitations and decay times they are due to distinct crystallographic iron centers. This is also supported by Mössbauer measurements. From the characteristics of the UV excitations shown in Fig. 2, one can assign these to charge-transfer (CT) transitions (*13*). As can be seen in this figure, the intensity of the CT transition associated with the 758-nm emission is dependent on the thermal treatment of the samples. It was also observed that samples prepared with a long annealing time exhibit an irreversible decrease in the width of the UV excitation of the 758-nm band at room temperature when they were *previously cooled* below room temperature. Thus the results presented in Fig. 3 are related to an irreversible thermal effect. This effect also decreases the UV bandwidth excitation of the 758-nm band.

The luminescent features presented in Fig. 3 are unusual for TM-impurity spinel-like phosphors, for which it is not expected that irreversible bandshape changes can be due to cooling near or below room temperature. In the present case these features can be associated to the following observed trends: (a) the 758-nm emitting centers are formed at the beginning of the sample synthesis and their relative number have a significant probability of being reduced at low temperature after the sample has previously been submitted to long high-temperature annealing times; (b) the 705-nm emitting centers need long annealing times for their formation and their relative number has a measurable increase after pre-cooling below room temperature if the sample was submitted to long high-temperature annealing times. These trends imply that a fraction of the 758-nm centers become 705-nm centers in two steps: one during the annealing at high temperature and another during cooling below room temperature.

Two diffusion mechanisms will be considered here to account for the above mentioned trends: One that occurs at sintering (or annealing) temperature, as generally expected when the host lattice has inequivalent sites (or vacancies) and a second, low-temperature ionic diffusion process, usually not considered for high melting-point oxides (*16*). The second diffusion process cannot be described by an Arrhenius equation with a constant potential barrier (or activation energy). Since the activation energy required for the low-temperature diffusion mechanism is not compatible with that expected for the spinel blocks of the compound, the 758-nm centers should be located in the inter-spinel block region, that is, in BR sites. If a second diffusion mechanism exists, a significant fraction of the 705-nm centers should be placed near the boundary of the spinel blocks (that is, Al(3) sites) to account for a diffusion between these two centers. The observed excitation spectra support these last two assignments.

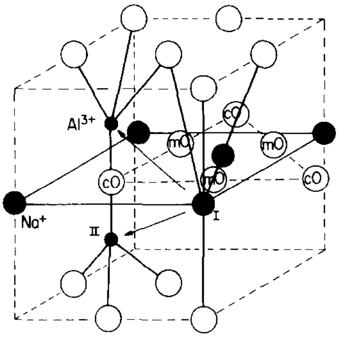

FIG. 4. Part of the interspinel block space. I and II are the Na (Beevers-Ross) and Al(3) sites, respectively. The arrows indicate the proposed low-temperature iron diffusion. cO are column oxygen and mO are mid-oxygen interstitial sites.

In the following discussion we shall denote these sites as I and II, respectively (Fig. 4). If iron ions transfer from site I to site II due to a high-temperature diffusion process, one would then need to consider two distinct situations to explain the results shown in Fig. 3. The short-dashed spectrum of Fig. 3 can be associated with Fe in I sites with a negligible jump probability into vacant next-neighboring II sites. The long-dashed and full-line spectra of Fig. 3 would be associated with Fe(I) centers having a significant jump probability to vacant sites II (denoted as Fe(I′) here). The vacant II probability of occupation of the sites should decrease with the annealing time because annealing causes sodium losses, thus reducing the necessary number of vacant Al(3) sites required to stabilize the structure by charge compensation. F(I′) to Fe(II) jumps can provide part of the negative charge reduction in the spinel blocks. The luminescent results shown in Fig. 3 can thus be understood as a low temperature diffusion of Fe(I) ions to II sites (where they remain trapped) when mobile Fe(I) ions reach I′ sites during their diffusion through the conduction plane. In Fig. 4 is shown a graphic representation of this interpretation. The arrows in this figure indicate the proposed Fe(I) to Fe(II) diffusion. The possibility of having the emitting centers located at mO sites is discarded because the Fe(II) excitation spectra show that they must be in sites typical of spinel blocks. Furthermore one should not expect to observe luminescence from Fe ions in mO sites.

To explain the migration of Fe(I) to II sites one can make the following model. Consider the $NaAl_{5-x}Fe_xO_8$ lattice with Fe ions in both BR sites and in Al(3) sites, and vacancies in BR sites and in sites inside the spinel blocks. Consider further that E_V, E_I, and E' are the activation energies for vacancy formation inside Al(3) sites, for Fe(I) transport through BR sites, and for the Fe(I′) to II sites jump, respectively. The diffusion must depend on (i) probability of having vacancies in Al(3) sites, assumed proportional to $\exp(-E_V/kT_A)$, where T_A is the annealing temperature; (ii) the probability of the Fe(I) ions to find I′ sites, which would be proportional to $\exp(-E_I/kT)$; and (iii) the probability of Fe(I′) ions jump into II sites, which should be proportional to $R \exp(-E'/kT)$. R is a parameter dependent on the Al(3) sites occupation allowed by the charge compensation of the structure. That is, R should be dependent on the sodium loss, thus on both the annealing time and temperature, and also on the initial Na/Al stoichiometry of the sample. The trapping of the Fe ions in II sites implies that the diffusion process should relax after some time.

The diffusion increase at low temperature, proposed from the results shown in Fig. 3 is a process that cannot be described by the Arrhenius-type equations described above (*17*). However, if one assumes that its activation energy, E', is a function of the temperature of the form $E' \simeq T^{n+1}$, with $n \geq 0$, then that increase could be understood. In a classical view this assumption means that there is a potential barrier dependent on the vibrations of the Fe(I′) and the surrounding ions near Al(3) sites, that is, a potential barrier proportional to the effective volume displayed by the ions. With this hypothesis the diffusion rate of Fe(I′) to II sites, would the be controlled by $\exp(-\text{const.}\ \sqrt{T})$.

Acknowledgments

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References

1. J. T. Kummer, *Prog. Solid State Chem.* **7,** 141 (1972).
2. G. Yamaguchi and K. Suzuki, *Bull. Chem. Soc. Jpn.* **41,** 93 (1968).
3. M. Bettman and C. R. Peters, *J. Phys. Chem.* **75,** 1774 (1969).
4. C. Collin, J. P. Boilot, A. Kahn, J. Thery, and R. Gomes, *J. Solid State Chem.* **21,** 283 (1977).
5. A. K. Ray and E. C. Subbarao, *Mat. Res. Bull.* **10,** 583 (1975).
6. J. Thery and D. Briancon, *Rev. Hautes Tem. Refractaires* **1,** 221 (1964).
7. D. Wolf, "Fast Ion Transport in Solids—Proceedings of the International Conference" (P. Vaiskista, J. N. Mundy, and G. K. Shenoy, Eds.), p. 342, 1979, Lake Geneva, Wisconsin.
8. M. Harata, *Mat. Res. Bull.* **6,** 461 (1971).
9. G. C. Farrington, B. Dunn, and J. O. Thomas, *Appl. Phys. A* **32,** 159 (1983).
10. L. Abello, S. J. Schwerdtfeger, and C. F. Schwerdtfeger, *Solid State Commun.* **44,** 497 (1982).
11. L. Abello, S. J. Schwerdtfeger, and C. F. Schwerdtfeger, *Phys. Status Solidi B* **125,** 333 (1984).
12. W. H. J. Stork and G. T. Pott, *J. Phys. Chem.* **78,** 2496 (1974).
13. J. Maria Neto, T. Abritta, F. de Souza Barros, and N. T. Melamed, *J, Lumin.* **22,** 109 (1981).
14. J. R. Akridge, B. Srour, C. Meyer, Y. Gros, and J. H. Kennedy, *J. Solid State Chem.* **25,** 169 (1978).
15. F. J. Verwey and E. L. Heilmann, *J. Chem. Phys.* **15,** 174 (1947).
16. M. J. L. Sangster and A. M. Stoneham, *J. Phys. C* **17,** 6093 (1984).
17. Y. M. Kagan, "Defects in Insulating Crystals" (V. M. Tuchkevich and K. K. Shuarts, Eds.), p. 17, Springer-Verlag, Berlin, 1981.