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THE MULTIVALENT β″-ALUMINAS

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The Multivalent β" Aluminas

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ABSTRACT

The multivalent β"-aluminas are a rich and diverse family of fast ion conductors. Their potential applications range from the traditional (batteries and sensors) to the unexpected (optoelectronic devices and lasers). This paper briefly reviews the preparation and properties of β"-aluminas containing Pb(II), Nd(III), and Cu(I) ions.

1. INTRODUCTION

The study of β and β"-alumina is closely associated with the development of solid state ionics. Yao and Kummer's observation [1] that sodium beta alumina has a sodium ion conductivity at room temperature comparable to that of aqueous NaCl stimulated widespread interest in the topic of fast ion transport in solids and led to extensive efforts to develop the sodium/beta alumina/sulfur

battery, one of the first new technologies made possible by high conductivity solid electrolytes. Since Yao and Kummer's work, interest in the ß and ß"-aluminas has endured, principally because of their ability to undergo ion exchange reactions in which the sodium ion content is replaced by a wide variety of monovalent, divalent, and trivalent cations. Thus, the ß and ß"-aluminas are not single compounds, but a diverse family of solid electrolytes with a wide range of characteristics and potential applications - from high energy density batteries to lasers.

Kummer [2] first described the remarkable ion exchange properties of sodium ß-alumina. More recent investigations by the present authors demonstrated that the ion exchange chemistry of sodium ß"-alumina, whose structure is very similar to that of sodium ß-alumina, is actually quite different and richer than that of sodium ß-alumina. While the sodium ion content of ß alumina readily exchanges only with monovalent cations, the sodium ion content of ß"-alumina can be exchanged for virtually any +1, +2, or +3 cation in the periodic chart [3, 4, 5], which demonstrates that fast cation transport in solids is not limited to a few monovalent cations, but, in the right structure, can be observed for many different cations.

The divalent and trivalent ß"-aluminas include many different compounds with unexpected properties. Among them are Pb(II) ß"-alumina, which has an ionic conductivity comparable to that of Na(I) ß"-alumina and develops electronic conductivity upon heating in vacuum; Nd(III) ß"-alumina, of interest as a new solid state laser material; and ß"-alumina containing Cu(I), which may prove to be a tunable laser host. This paper presents a brief overview of the ß"-aluminas just mentioned, which are only a few representatives of this fascinating family of materials.

2. PREPARATION OF THE MULTIVALENT ß"-ALUMINAS

The first unambiguous evidence that divalent ions can diffuse rapidly in ß"-alumina was presented by Dunn and Far y.)n [3,4], who reported the synthesis and ionic conductivities of Ba(II), Cc'" and Sr(II) ß"-alumina. Later work demonstrated that trivalent ions can also replace the Na(I) ions in ß"-alumina and are, as expected, considerably less mobile than monovalent or divalent ions in the structure [5]. Among the ions known to exchange for Na(I) in ß"-alumina are: the monovalent cations of K, Ag, Tl, and Cu [2]; the divalent

cations of Ca, Sr, Ba, Zn, Cd, Pb, Mn, Eu, Ni, Co, Sn, Hg, and Sm [6]; and the trivalent cations of Gd, Nd, Eu, Yb. Sm, Tb, Bi, Cr, and Er [6].

Ion exchange reactions are typically carried out at 200-600°C in a pure molten salt of the exchanging ion, a mixed molten salt of the exchanging cation and sodium ions, or by a gas phase reaction in which the crystal to be exchanged is buried in or suspended over a salt of the exchanging ion and heated to a temperature below the melting point of the salt. The gas phase technique is especially useful for attaining high levels of exchange with minimal crystal damage. Sattar et al. [6] have presented a more complete discussion of the ion exchange process.

3. Pb(II) ß"-ALUMINA

Pb(II) ß"-alumina is exceptional among the divalent isomorphs of ß"-alumina in that its ionic conductivity at room temperature is comparable to that of sodium ß"-alumina (about 10^{-3} (ohm-cm)$^{-1}$). Most divalent ß"-aluminas have room temperature conductivities several orders of magnitude lower than that of the sodium form. What is even more surprising is that Pb(II) ß"-alumina transforms from a colorless electronic insulator to a purple electronic conductor when heated in vacuum and reverts to its initial state when subsequently heated in air. In fact, Ag(I), Pb(II), and Bi(III) ß"-alumina undergo similar reactions. When each is heated in an atmosphere with a low partial pressure of oxygen, a color change occurs which is sometimes accompanied by an insulator to semiconductor transition. This behavior was first observed and described by Rohrer et al. [7].

Rohrer et al. have shown that the coloration of Pb(II) ß"-alumina proceeds from the edges of the crystal along the high-conductivity conduction planes, as does the bleaching reaction that occurs when colored samples are heated in air. A reasonable explanation for both processes involves the reversible loss of oxygen from the structure. Most likely the column oxygens (O(5)) are the species principally involved in the reaction. In Kroger-Vink notation:

$$O_O \rightarrow V_O^{\bullet\bullet} + 1/2 O_2 + 2e^-$$

The two electrons left behind for each oxygen removed presumably are trapped in the conduction plane rather than the spinel block, since electrons should be

more easily accommodated in the conduction plane, where high ion mobilities allow greater lattice polarization.

The colored samples of Pb(II) ß"-alumina also exhibit electronic conductivity, which can vary over six orders of magnitude, the upper limit being approximately 5×10^{-3} (ohm-cm)$^{-1}$. Direct current measurements indicate that the conductivity is ohmic and impedance spectra show frequency independent conduction at low frequencies. The magnitude of the electronic conductivity is very sensitive to the details of sample preparation. Samples which have comparable conductivities are only produced when several crystals are treated as similarly as possible.

The defect structure of Pb(II) ß"-alumina is quite complex. The model for defect creation proposed by Rohrer et al., involving the reversible loss of oxygen from the conduction planes, has the rather intriguing implication that Pb(II) ß"-alumina may be a relatively fast ion conductor for oxygen ions as well as Pb(II) ions. Further studies to understand the nature of this reaction and of oxygen ion motion in the structure are underway.

4. THE LANTHANIDE ß"-ALUMINAS

The first preparation of the lanthanide ß"-aluminas stimulated exploration of the spectroscopy and optical properties of the divalent and trivalent ß"-aluminas. Spectroscopy studies can provide a great deal of information about about local ion environments. In addition, the lanthanide ß"-aluminas are of considerable interest for their potential applications. Several lanthanide and transition-metal substituted ß"-aluminas have novel optical characteristics; selected compositions have already been shown to lase. Ion exchange is a particularly advantageous preparation technique for opto-electronic crystals, because the doping process is separate from the process of crystal growth. Consequently, the valence of the dopant ion as well as its spatial distribution can be more precisely controlled in single crystals of ß"-alumina than in traditional materials. Following is a brief summary of some of the more significant results obtained for Nd(III) and Cu(I)-exchanged ß"-aluminas.

4.1 Nd(III) ß"-Alumina

Optical absorption spectroscopy and ESR have been used to study the site occupations for Nd(III) in ß"-alumina as a function of Nd(III) concentration [8]. Absorption spectra taken at 4K indicate that Nd(III) is present in two sites. ESR measurements indicate that mid-oxygen occupation predominates. Complementary studies by Queenan and Davies [9] found that the distribution of Nd(III) in mO and BR sites can be influenced by the conditions of thermal annealing. Recent X-ray diffraction results of Carrillo-Cabrera et al. [10] show that the column oxygens are displaced towards BR sites and the Nd(III) ions relax locally along the conduction pathways towards adjacent BR sites.

One important feature of the absorption spectrum of significance for potential applications is the presence of an anomalously large absorption coefficient at 575 nm [11]. This absorption arises from the hypersensitive $^4I_{9/2}$ → $^4G_{5/2}$, $^2G_{7/2}$ transition. The oscillator strength of the transition (6×10^{-5}) is nearly ten times that observed in Nd:YAG (7×10^{-6}), while the other transitions have comparable oscillator strengths.

The fluorescence lifetime of Nd(III) in ß"-alumina is also unusual [11]. First, this lifetime is in the range of 400 µsec, which is nearly twice as large as commonly observed for Nd:YAG ($Y_3Al_5O_{12}$). Second, there is no evidence of fluorescence quenching even at concentrations as large as 1×10^{21} Nd(III)/cm^3. In contrast, Nd: YAG exhibits concentration quenching at Nd(III) concentrations of 1 to 2×10^{20} ions/cm^3.

The spectroscopic properties of Nd(III) ß"-alumina suggest that this material may be of considerable interest for optical devices. Jansen et al. [11] have already achieved lasing in both pulsed and cw modes using small single crystals of ß"-alumina containing from 4 to 7×10^{20} Nd(III)/cm^3. What is remarkable is that the gain/cm achieved by pumping the 575 nm band is approximately ten times greater in ß"-alumina than in a Nd:YAG laser pumped with a flashlamp. This suggests that it should be possible with Nd(III) ß"-alumina crystals to achieve lasing in crystals of very small volume, a feature of considerable interest for a variety of applications.

4.2. Cu(I) ß"-Alumina

The spectroscopy of Cu(I) is particularly interesting because of its emission in the blue-green part of the spectrum. Howe er, obtaining Cu(I) in a usable laser host material has been difficult because traditional crystal growth processes invariably oxidize the Cu(I) to Cu(II), which interferes with and usually quenches the Cu(I) luminescence. Using ion exchange processes, however, Barrie et al. [12] were able to control the valence of copper and to produce ß"-alumina crystals containing $\approx 10^{19}$ Cu(I)/cm^3. The resulting materials showed broad green luminescence peaked at 535 nm.

A noteworthy feature of Cu(I) ß"-alumina is that its emission can be tuned over much of the visible spectrum [12]. This is possible because the c-lattice parameter of ß"-alumina can be varied [4] by preparing crystals with small concentrations of Cu(I) and different majority ions, the latter determining the lattice parameter. Preliminary investigations suggest that Cu(I) ß"-alumina not only may lase, but also be a laser host whose output is tunable.

5. CONCLUSIONS

The results described in this paper are only a small selection from the diverse studies of ion transport, structure, thermochemistry, and spectroscopy carried out on various multivalent ß"-aluminas. Other work underway or recently completed includes investigations of ion ordering in mixed Na(I)-Eu(II) ß"-aluminas [13-14], the hydration chemistry of the divalent ß"-aluminas [15], more thorough explorations of the spectroscopy of the lanthanide ß"-aluminas and their potential applications [16-19], and rather elegant simulations of local ion distribution and motion in the ß"-aluminas by means of molecular dynamics [20]. All this work should leave at least one impression on the reader: that the ß"-aluminas are a rich and intriguing family of materials, arguably the most varied of all high conductivity solid electrolytes. They include both some of the first high conductivity solid electrolytes studied and some of the freshest and brightest. It is just possible that a major solid state ionics technology may be in novel opto-electronic devices, far from the roots of the field in batteries, but linked to them by the common exploitation of materials which support fast ion transport in the solid state, albeit in the case of lasers, with some rather unusual ions.

6. ACKNOWLEDGEMENTS

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