

ELECTRONIC CONDUCTIVITY IN Pb(II)- β "-ALUMINA

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Received 4 August 1987; in revised version 15 December 1987

Pb(II)- β "-alumina is one of several divalent isomorphs of the well-known fast ion conductor, Na(I)- β "-alumina. When Pb(II)- β "-alumina is heated in vacuum, it transforms from a colorless electronic insulator to a purple electronic conductor. When heated in air, it returns to the initial state. The electronic conductivity is temperature activated and the color is due to broad but discrete absorptions in the visible range. This paper will discuss the factors that are important to the coloring process, as well as possible mechanisms for the formation of defects and electronic conduction.

1. Introduction

A wide range of multivalent β "-alumina isomorphs may be produced by the ion exchange of Na(I)- β "-alumina. It has been suggested that in some isomorphs, vacuum heating causes oxygen loss from the structure and subsequent reduction of the metal cations [1]. For example, in Eu(III)- β "-alumina, vacuum heating causes a change in fluorescence which indicates that Eu(III) ions have been reduced to the Eu(II) state [2].

We have found that when Ag(I), Pb(II), or Bi(III)- β "-alumina is heated in an atmosphere with a low partial pressure of oxygen, there is a color change which is sometimes accompanied by an insulator to semiconductor transition. In each case, the change in optical and electrical properties can be reversed by heating the crystal in air. This paper describes the factors which influence defect formation in Pb(II)- β "-alumina and the new properties that result from the formation of these defects.

2. Experimental

Pb(II)- β "-alumina is easily prepared by immersing a single crystal of Na(I)- β "-alumina in molten PbCl₂ at 500°C [3]. In a short time, all of the Na(I) ions are replaced by Pb(II) ions and the new com-

position of the crystal is Pb_{0.83}Mg_{0.67}Al_{10.33}O₁₇. Crystals with lower Pb(II) concentrations can be made by interrupting the ion exchange process before completion. The extent of exchange can be monitored with a ²²Na tracer. After ion exchange, crystals are still clear, colorless, and free of cracks.

Although samples were successfully colored in three different ways, vacuum heating was the primary method. The results reported here come from samples colored in this way. Crystals were sealed in evacuated quartz ampoules and heated to specific temperatures. The temperature range investigated was 300-900°C, the annealing time was typically 24 h and the air pressure in the ampoule was approximately 8 μ Hg. Although most of the samples were pure Pb(II)- β "-alumina, samples in the composition range Na_xPb_{0.83-x/2}Mg_{0.67}Al_{10.33}O₁₇ (where 0 < x < 0.167) were also studied. Following the heating, samples were quenched to room temperature either by removing the ampoule from the furnace and placing it directly onto a cool surface or by immersing it in cool water. We observed the same coloring reaction when crystals were heated in dry argon or forming gas (15% H₂ 85% N₂). The color could be removed from the crystal (bleached) by heating it in air.

Optical absorption measurements were made with a Cary 14 spectrophotometer or a Perkin-Elmer lambda 4C spectrophotometer. Low temperature

measurements were made using an Oxford Instruments liquid nitrogen cryostat. The absorption was measured parallel to the c -axis. The Pb(II)- β'' -alumina platelets used for optical measurements were 0.1 to 1.0 mm thick, along the c -axis.

Electronic conductivity measurements were made using an automated frequency response analysis system (Solarton 1250 frequency response analyzer controlled by a Hewlett-Packard series 9000 computer). Contacts to the crystal were made by sputtered gold alone, silver paint alone or silver paint over sputtered gold. The crystals used for conductivity measurements were cut into rectangular platelets and contacts were applied to opposing faces of the sample, perpendicular to the conduction planes. The conductivity was measured in the frequency range 1 mHz to 65 kHz and the temperature range 77 to 450 K.

3. Results and discussion

We have observed that the color proceeds only from the edges of the crystal that are perpendicular to the conduction planes. Likewise, when a sample is bleached the colorless areas start at these same edges. This indicates that optically active defect species are formed at the interface between the crystal and the surrounding atmosphere and that these defects then diffuse into the crystal via the conduction planes. Since the defects are formed when the crystal is heated in an atmosphere with a low partial pressure of oxygen, and removed when the sample is heated in air, it is likely that oxygen is lost from the structure during vacuum heating. At 600°C, the colored region can spread across several millimeters of crystal in several minutes. This implies the rapid motion of oxygen ions to the interface. Although there is no detectable weight loss during the coloring reaction, the limit of the gravimetric measurement fixes the maximum oxygen loss to less than 0.01% of the total oxygen content.

We have examined the electron spin resonance (ESR) spectra of colored and bleached samples from 4 K to room temperature. The only paramagnetic resonance signal detected could be attributed to Mn(II) impurities. These impurities were present in colored and bleached samples, as well as unex-

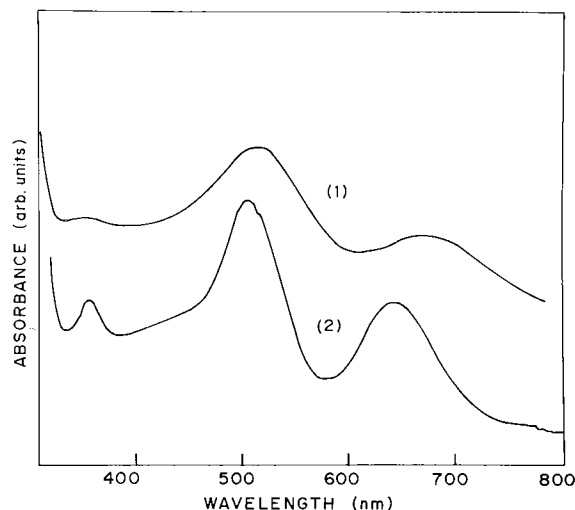


Fig. 1. Optical absorption of vacuum annealed Pb(II)- β'' -alumina at (1) 293 K and (2) 77 K.

changed Na(I)- β'' -alumina. Therefore, the defects in colored Pb(II)- β'' -alumina are spin paired.

Fig. 1 shows the optical absorption of Pb(II)- β'' -alumina after being vacuum heated at 670°C for 18 h. Three distinct peaks are clearly seen. In addition to these, there is a fourth peak at 450 nm which is obscured by the large absorption at 520 nm. All the absorption peaks narrow and shift to higher energies as the temperature is decreased to 77 K. This shift is due to the decreasing lattice parameters. As the space to which the defect is confined shrinks, the energy of the excited state becomes larger.

Fig. 2 shows the optical absorption of samples which have been vacuum heated for at least 20 h at various temperatures and then quenched to room temperature. There appear to be five separate peaks in some of the spectra. The peak which occurs between 500 nm and 600 nm (d) shifts steadily with annealing temperature. The positions of the three highest energy peaks (a, b, c) remain nearly the same with annealing temperature; however, the relative intensities change. The changes in intensity of different absorptions may reflect relative stabilities of different defect species at different annealing temperatures.

Electronic conductivity is present in some colored samples of Pb(II)- β'' -alumina. Direct current measurements show that the conductivity is ohmic and impedance spectra show frequency independent

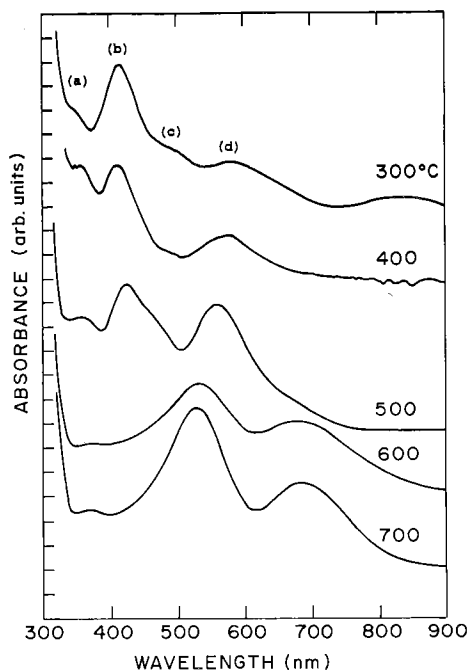


Fig. 2. Room temperature optical absorption of Pb(II)- β'' -alumina after vacuum heating at various temperatures.

conduction at low frequencies. Fig. 3 shows the variation of the electronic conductivity with temperature for a sample vacuum heated at 650°C for 8 h. The ionic conductivity, which depends on the ther-

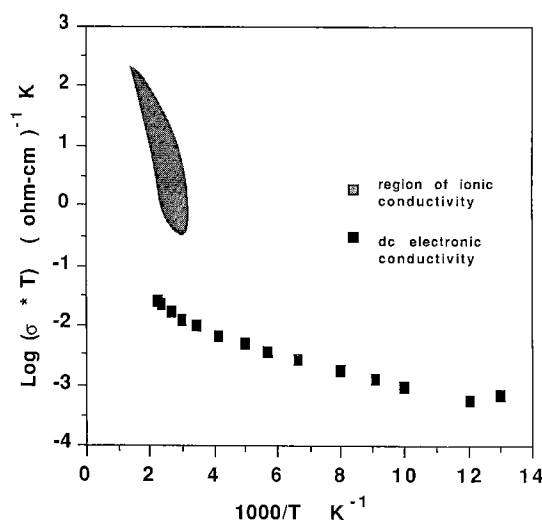


Fig. 3. Electronic and ionic conductivity of Pb(II)- β'' -alumina. The ionic conductivity, which is dependent on the thermal history of the sample, is indicated by the shaded region.

mal history of the sample, is shown for comparison [4]. The conductivity increases with increasing temperature, but the Arrhenius plot is not linear. The increase in conductivity with temperature indicates that an electron hopping model may be applicable. Also, the increasing activation energy with increasing temperature indicates that polaron formation may be important. Since the ESR silence indicates that all of the defects are spin paired, the charge carriers are most likely bipolarons.

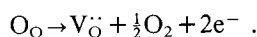
We have found that the electronic conductivity is very sensitive to sample preparation. The electronic conductivity in colored samples can vary over six orders of magnitude, with the upper limit being approximately $5 \times 10^{-3} (\Omega \text{ cm})^{-1}$. Samples with similar properties can be prepared only when they are treated together, in the same ampoule. Partial bleaching at the edges of crystals is often visible after the quench. This occurs because of the rapid reabsorption of oxygen and annihilation of defects around the edges of the crystal during cooling. This may create resistive barriers at the edges which do not reflect the bulk properties of the crystal. Therefore, the large variation in the magnitude of electronic conductivity may be the result of inhomogeneous defect distribution in the crystal. The degree of inhomogeneity would be determined by the quench rate and the temperature from which the sample is quenched.

The factors which affect the optical absorption spectrum and electronic conductivity are:

- (1) the temperature at which the crystals are annealed,
- (2) the rate at which the crystal is quenched,
- (3) the partial pressure of oxygen in the atmosphere,
- (4) and the amount of residual sodium left in the crystal.

A systematic study of the influences of these factors on the properties of Pb(II)- β'' -alumina is in progress. In general, higher annealing temperatures, lower partial pressure of oxygen, and less residual sodium lead to increased optical absorption.

The proposed model for the coloring reaction is based on oxygen loss from the β'' -alumina framework. It is likely that the so-called column oxygens (O(5)) are the species principally lost from the structure. In Kröger-Vink notation:



The two electrons that are left behind for each oxygen removed presumably become trapped in the conduction plane rather than the spinel block. Electrons can be more easily accommodated in the conduction plane, where high ion mobilities allow greater lattice polarization.

It is likely that the defect structure of Pb(II)- β "-alumina is quite complex. The discrete nature of the optical absorptions indicates that some of the defects have bound excited states with energies of about 2 eV. The electronic conduction, on the other hand, indicates that there are charges which are free to hop from site to site with very little thermal activation. Singly charged defects must be excluded because of the ESR silence, and the Pb(0) defect (which has been studied in alkali halides) does not have absorptions at the correct energies to account for the optical absorption spectrum. [5] Oxygen vacancies and Pb(II) cations are possible traps for electrons and aggregations of these species may be responsible for the observed properties.

4. Conclusions

We have found that when Pb(II)- β "-alumina is heated in an atmosphere with a low partial pressure of oxygen, it becomes colored and, in some cases, semiconducting. The physical properties are very sensitive to the conditions used for the coloring. Fur-

ther studies are required to understand the relationship between the optical and electronic properties and the preparation conditions. We have proposed a model for defect formation based on the loss of oxygen from the conduction planes. This model, together with the observation of rapid defect formation implies that Pb(II)- β "-alumina may be a fast ion conductor for oxygen ions as well as Pb(II) ions.

Acknowledgement

This research was funded by the Office of Naval Research. Additional support from the National Science Foundation, Materials Research Laboratory Program, under Grant No. DMR-8519059 is gratefully acknowledged. The authors specially thank Dr. E.C. Venturini of Sandia National Laboratories for his assistance in ESR spectroscopy.

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