

Phase equilibria in the system CdO-B₂O₃-SiO₂ at 800° C

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Phase equilibria in the system CdO-B₂O₃-SiO₂ were investigated at 800° C using X-ray powder diffraction techniques. The binary phases reported previously were confirmed, but no ternary phases were found. Solid solution effects were investigated for the primary and binary phases by comparison of patterns; no solid solutions were detected. The relationship of the phase diagram to the composition of photoconductive oxide glasses is discussed and suggestions are made of possible mechanisms responsible for the photoelectric effects.

1. Introduction

The existence of electronic conduction in glasses containing a variable valency ion has been demonstrated by several authors [1-4]. More recently Strickler and Roy [5] have found a new family of photoconducting oxide glassy materials containing no variable valency ions. Their study was limited to systems capable of yielding glasses with a high concentration of heavy metal oxide, this being one of the requirements for Goodenough's hypothesis [6] of conduction in certain metal oxides. Investigation showed that the highest photocurrents were obtained from compositions grouped around the general formula 65 mol% MO-20 mol% R₂O₃-15 mol% XO₂ and in particular from the systems CdO-B₂O₃-SiO₂ and CdO-B₂O₃-GeO₂. Electron microscope studies [5, 7] showed that the glasses examined had a diphasic nature whilst Čáslavská *et al.* [8] attempted to optimize the photoconductivity in the system CdO-B₂O₃-SiO₂ by adding small percentages (by weight) of cadmium oxide to compositions of the general formula given above. They found that the most photoconductive composition studied corresponded to 79.42 wt% CdO-12.49 wt% B₂O₃-8.09 wt% SiO₂ with the second most photoconducting at 79.66 wt% CdO-12.34 wt% B₂O₃-8.00 wt% SiO₂; they then proceeded to postulate two possible hypotheses to explain the photoconduction. The present study was undertaken to provide further evidence concerning

these hypotheses and at the same time determine the complete phase equilibrium diagram at 800° C.

1.1. Previous work

The ternary system has not been investigated at any temperature but data exists for all of the binary systems concerned.

From a partial study of the CdO-B₂O₃ system, Mazetti and de Carli [9] reported the existence of two phases: 2CdO.3B₂O₃ and CdO.B₂O₃, while Botden and Kröger [10] reported the existence of four cadmium borates; 2CdO.3B₂O₃. CdO.B₂O₃, 2CdO.B₂O₃ and 3CdO.B₂O₃. However, neither of these investigations reported any X-ray data.

Subbarao and Hummel [11] investigated the entire cadmium oxide-boric oxide phase diagram using differential thermal analysis and X-ray powder techniques. They reported the existence of four intermediate phases 2CdO.3B₂O₃, 3CdO.2B₂O₃, 2CdO.B₂O₃ and 3CdO.B₂O₃. The last two were claimed to be dimorphic with transition temperatures of 900° C and 870° C respectively. X-ray diffraction data were reported for all phases, but the patterns for 3CdO.2B₂O₃ and 2CdO.B₂O₃ were very similar. The existence of the compound CdO.B₂O₃ claimed previously [9, 10] could not be confirmed.

Subsequently Hart and Steward [12] investigated these compounds in the temperature range 725 to 850° C using X-ray examination, differential

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thermal analysis and high temperature microscopy. They concluded that the compound $3\text{CdO}\cdot 2\text{B}_2\text{O}_3$ could not be prepared; the X-ray data they report for the other three phases are similar but not identical to those given by Subbarao and Hummel [11].

Finally Hand and Krogh-Moe [13] reported the existence of $\text{CdO}\cdot 2\text{B}_2\text{O}_3$ and showed that there were no other phases between this and $2\text{CdO}\cdot \text{B}_2\text{O}_3$. X-ray data are given for both $\text{CdO}\cdot 2\text{B}_2\text{O}_3$ and $2\text{CdO}\cdot \text{B}_2\text{O}_3$; those for the latter are in very good agreement with those of Hart and Steward [12]. As single crystals of $\text{CdO}\cdot 2\text{B}_2\text{O}_3$ and $2\text{CdO}\cdot \text{B}_2\text{O}_3$ were grown from melts of composition $2\text{CdO}\cdot 3\text{B}_2\text{O}_3$ and $3\text{CdO}\cdot 2\text{B}_2\text{O}_3$ respectively, this would appear conclusive.

Subsequently the crystal structure of $\text{CdO}\cdot 2\text{B}_2\text{O}_3$ was determined [14], thus removing any doubts that the chemical composition could be incorrect. Thus it appears that the only cadmium

borates which exist are $\text{CdO}\cdot 2\text{B}_2\text{O}_3$, $2\text{CdO}\cdot \text{B}_2\text{O}_3$ and $3\text{CdO}\cdot \text{B}_2\text{O}_3$.

It would appear that the phase equilibrium diagram for the cadmium oxide—silicon dioxide system has not been fully determined. Three intermediate phases have been reported in a partial study [15], these being $\text{CdO}\cdot \text{SiO}_2$, $2\text{CdO}\cdot \text{SiO}_2$ and $3\text{CdO}\cdot \text{SiO}_2$. The X-ray data for the first of these agreed with those in the X-ray Powder Data File (2-0719) with the exception of a line at 4.07 Å. This line was not observed and could be attributed to the strongest reflection of cristobalite. Fresh data were included for the other two compounds.

In the phase system boric oxide—silicon dioxide, there are no intermediate phases or solid solutions [16]. X-ray powder diffraction data exist in the X-ray Powder Data File for the primary oxides in this system. However, since the melting point of boric oxide is 450°C [17], it is a liquid at the investigating temperature.

TABLE I Specimens prepared, chemical composition and X-ray analysis

| Specimen no. or compound | Chemical composition (wt%) | | | Phase analyses | | |
|------------------------------------|-------------------------------|-------------------------------|------------------|--|------------------------------------|------------------------------------|
| | CdO | B ₂ O ₃ | SiO ₂ | Major | Minor | Trace |
| CdO·2B ₂ O ₃ | 48.0 | 52.0 | | CdO·2B ₂ O ₃ | | 2CdO·B ₂ O ₃ |
| | 43.0 | 57.0 | | CdO·2B ₂ O ₃ | | |
| 2CdO·B ₂ O ₃ | 79.0 | 21.0 | | 2CdO·B ₂ O ₃ | | |
| 3CdO·B ₂ O ₃ | 84.7 | 15.3 | | β-3CdO·B ₂ O ₃ | | CdO |
| CdO·SiO ₂ | 68.0 | | 32.0 | CdO·SiO ₂ | | |
| 2CdO·SiO ₂ | 81.0 | | 19.0 | 2CdO·SiO ₂ | | |
| 3CdO·SiO ₂ | 86.5 | | 13.5 | 3CdO·SiO ₂ | | CdO |
| 1 | | 55 | 45 | * see below | | |
| 2 | 10 | 25 | 65 | CdO·2B ₂ O ₃ + α-quartz | | |
| 3 | 30 | 55 | 15 | CdO·2B ₂ O ₃ | | α-quartz |
| 4 | 17 | 18 | 65 | CdO·2B ₂ O ₃ + α-quartz | | |
| 5 | 39 | 43 | 18 | CdO·2B ₂ O ₃ | | α-quartz |
| 6 | 43 | 22 | 35 | 2CdO·B ₂ O ₃ | CdO·2B ₂ O ₃ | α-quartz |
| 7 | 48 | 25 | 27 | 2CdO·B ₂ O ₃ | CdO·2B ₂ O ₃ | α-quartz |
| 8 | 45 | 35 | 20 | CdO·2B ₂ O ₃ | α-quartz | |
| 9 | 52.6 | 40 | 7.4 | CdO·2B ₂ O ₃ | | α-quartz |
| 10 | 60 | 35 | 5 | CdO·2B ₂ O ₃ | 2CdO·B ₂ O ₃ | |
| 11 | 30 | 10 | 60 | 2CdO·B ₂ O ₃ + α-quartz | | |
| 12 | 38 | 10 | 52 | 2CdO·B ₂ O ₃ + α-quartz | | |
| 13 | 61.8 | 16.5 | 21.7 | 2CdO·B ₂ O ₃ | α-quartz | |
| 14 | 70 | 18.6 | 11.4 | 2CdO·B ₂ O ₃ | | |
| 15 | 72 | 23 | 5 | 2CdO·B ₂ O ₃ | | |
| 16 | 30 | 2 | 68 | α-quartz + CdO·SiO ₂ | | |
| 17 | 55 | 10 | 35 | CdO·SiO ₂ | α-quartz | 2CdO·B ₂ O ₃ |
| 18 | 66.1 | 5 | 28.9 | CdO·SiO ₂ | | α-quartz |
| 19 | 68 | 10 | 22 | CdO·SiO ₂ | 2CdO·B ₂ O ₃ | |
| 20 | 70.5 | 5 | 24.5 | CdO·SiO ₂ | 2CdO·B ₂ O ₃ | |

TABLE I continued

| Specimen no. or compound | Chemical composition (wt %) | | | Phase analyses | | |
|-----------------------------|--------------------------------|-------------------------------|------------------|--|--|-----------------------|
| | CdO | B ₂ O ₃ | SiO ₂ | Major | Minor | Trace |
| 21 | 73.8 | 11.5 | 14.7 | 2CdO.B ₂ O ₃ + CdO.SiO ₂ | | |
| 22 | 75 | 6.7 | 8.3 | CdO.SiO ₂ | 2CdO.SiO ₂ | |
| 23 | 76 | 10 | 14 | CdO.SiO ₂ | 2CdO.SiO ₂ + 2CdO.B ₂ O ₃ | |
| 24 | 78 | 5 | 17 | 2CdO.SiO ₂ | 2CdO.B ₂ O ₃ | |
| 25 | 78 | 15 | 7 | 2CdO.B ₂ O ₃ | CdO.SiO ₂ | |
| 26 | 80 | 9 | 11 | 2CdO.SiO ₂ | 2CdO.B ₂ O ₃ | |
| 27 | 80 | 11 | 9 | 2CdO.SiO ₂ + 2CdO.B ₂ O ₃ | | |
| 28 | 79.5 | 12.4 | 8.1 | 2CdO.B ₂ O ₃ + 2CdO.SiO ₂ | | |
| 29 | 79 | 17 | 4 | 2CdO.B ₂ O ₃ | 2CdO.SiO ₂ | |
| 30 | 81.5 | 11 | 7.5 | β -3CdO.B ₂ O ₃ | 2CdO.SiO ₂ | |
| 31 | 82 | 12.9 | 5.1 | β -3CdO.B ₂ O ₃ | 2CdO.B ₂ O ₃ | |
| 32 | 82.2 | 5 | 12.8 | 2CdO.SiO ₂ | β -3CdO.B ₂ O ₃ | |
| 33 | 83.2 | 9 | 7.8 | β -3CdO.B ₂ O ₃ | 2CdO.SiO ₂ | |
| 34 | 84 | 5 | 11 | 3CdO.SiO ₂ | 2CdO.SiO ₂ + β -3CdO.B ₂ O ₃ | |
| 35 | 86 | 4 | 10 | 3CdO.SiO ₂ | β -3CdO.B ₂ O ₃ + CdO. | |
| 36 | 85.5 | 7 | 7.5 | 3CdO.SiO ₂ + β -3CdO.B ₂ O ₃ | | |
| 37 | 85 | 11 | 4 | β -3CdO.B ₂ O ₃ | | |
| 38 | 88 | 3 | 9 | 3CdO.SiO ₂ + CdO | β -3CdO.B ₂ O ₃ | |
| 39 | 90 | 5 | 5 | CdO + 3CdO.SiO ₂ | β -3CdO.B ₂ O ₃ | |
| 40 | 87 | 10 | 3 | CdO + β -3CdO.B ₂ O ₃ | | 3CdO.SiO ₂ |

* Mainly amorphous plus slight trace of crystalline material; probably α -quartz.

2. Experimental

The investigation was started by preparing the binary compounds and by examining a compact in the boric oxide-silicon dioxide system. The starting materials were; cadmium oxide, a Griffin certified reagent (not less than 99% pure), AnalaR boric acid (not less than 99.5% pure) and pure precipitated silica (Hopkin and Williams Ltd.). Quantities of silica and cadmium oxide were placed in separate crucibles and kept in the furnace at 800°C to drive off any water. They were only removed and allowed to cool ready for weighing when compacts were being prepared. The boric acid was not treated in this way. The amounts weighed were such as to give one-gram compacts after firing.

The compacts with high boric acid content were pre-fired. For these the appropriate quantities were mixed, ground to a fine powder and pressed for 5 min in a 1/2 in diameter steel die at 20 000 lb

in⁻². No binder was used. The compacts were then fired at 400°C for two or three hours, removed, re-ground and re-pressed for the final firing. Compacts with low boric acid content did not require pre-firing.

Both pre-firing and firing were carried out in air with the compacts in platinum boats. The temperature of the firing was controlled at 800 ± 5°C and the specimens air quenched.

Preliminary runs suggested that firing times were a minimum of three or four days to reach equilibrium, but a period of one week was found to be sufficient in all cases, and all compacts for which results are reported in Table I were fired for this length of time.

After firing, a little of the compact was ground and used as an X-ray powder specimen which was then examined in an 11.46 cm diameter Debye-Scherrer camera using filtered copper radiation.

3. Results

3.1. Cadmium oxide–boric oxide binary system

$\text{CdO} \cdot 2\text{B}_2\text{O}_3$: It proved difficult to produce a pattern of this phase alone at the nominal composition; there was always a trace of $2\text{CdO} \cdot \text{B}_2\text{O}_3$ present, presumably this is due to loss of boric oxide on firing (Section 3.3. below). Finally a compact with excess of boric oxide was made, the pattern from this agrees with that reported by Hand and Krogh-Moe [13].

$2\text{CdO} \cdot \text{B}_2\text{O}_3$: The present data agree with that of Hand and Krogh-Moe [13].

$3\text{CdO} \cdot \text{B}_2\text{O}_3$: The pattern obtained was not identical to either that of Subbarao and Hummel [11] for the β -form or that of Hart and Steward [12]. It fits the latter better at low diffraction angles but contains a few extra weak lines between 1.86 \AA and 2.38 \AA . These were not obtained by Hart and Steward [12], but were by Subbarao and Hummel [11]. The sample made also contained a trace of cadmium oxide.

3.2. Cadmium oxide–silicon dioxide binary system

$\text{CdO} \cdot \text{SiO}_2$: The data agree with the X-ray Powder Data File (2-0719) except that the lines at 7.53 \AA and 4.07 \AA were absent. The former was in a high background region of the film while the absence of the latter has been reported previously [14].

$2\text{CdO} \cdot \text{SiO}_2$: The data agree with that reported previously [14].

$3\text{CdO} \cdot \text{SiO}_2$: The pattern obtained agrees with that of Dent Glasser and Glasser [14] together with a trace of cadmium oxide.

3.3. Boric oxide–silicon dioxide binary system

The only binary compact prepared in this system confirms the previous work [16] that there is no intermediate phase. However, the present work suggests that the composition 55% boric oxide–45% silicon dioxide is mainly amorphous together with a trace of α -quartz, while previous work suggests that compositions containing more than 50% boric oxide are completely liquid. However, this discrepancy is not very significant due to the composition intervals of the firings in the original work [16] and the fact that boric oxide is volatile at temperatures above 700°C . According to Rockett and Foster [16] some 1.7% of boric oxide is lost from a pure sample after firing for 200 h at 730°C in an open platinum boat.

3.4. Thermal equilibrium diagram

During the course of the investigation into the thermal equilibrium diagram, eight binary and thirty-nine ternary compacts were made. Table I lists these compacts, composition, and interpretation of the X-ray diffraction patterns. The subsolidus compatibility triangles at 800°C consistent with these results are shown in Figs. 1 and 2.

X-ray powder patterns containing binary phases were compared. From this comparison there ap-

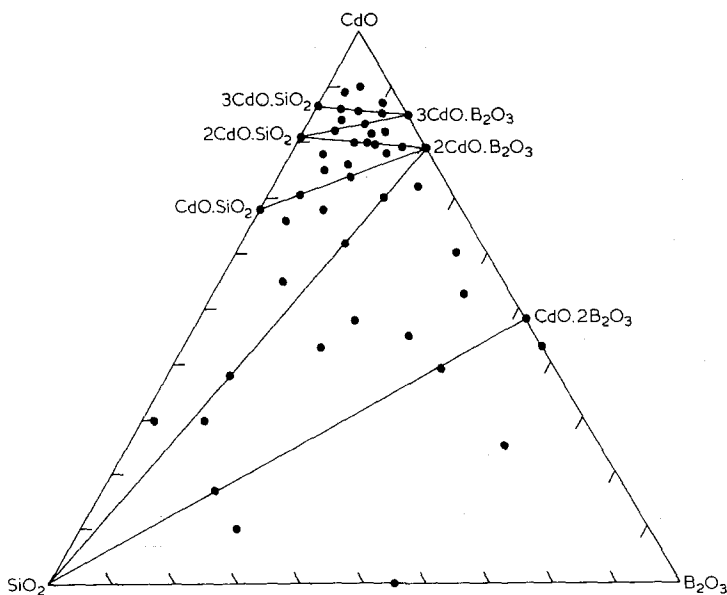
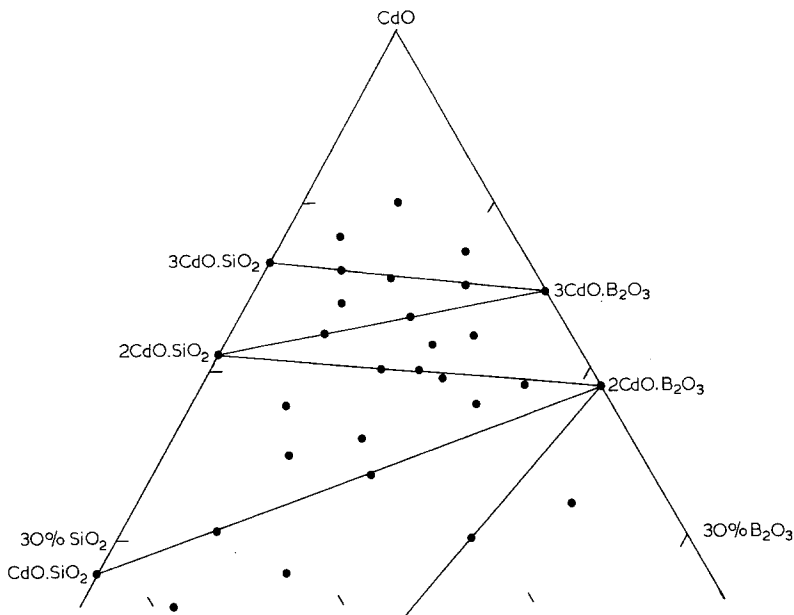


Figure 1 Phase equilibria in the system $\text{CdO}-\text{B}_2\text{O}_3-\text{SiO}_2$ at 800°C .

Figure 2 Phase equilibria in high cadmium oxide corner of the system $\text{CdO}-\text{B}_2\text{O}_3-\text{SiO}_2$ at 800°C .



peared to be no evidence of solid solution effects. Unfortunately most of the patterns lacked sharp lines in the back reflection region; because of this the limit of detection is poor and the existence of slight solubility cannot be discounted.

Boric oxide was not detected by X-ray diffraction in those compacts in which the chemical composition indicated that it should be present. This is no doubt due to its glassy nature after quenching (it melts at 450°C [17]), and Berger [18] has reported that it is very difficult to crystallize.

4. Discussion

The lack of solid solution, mentioned in the previous section, is not entirely unexpected. The published binary phase diagrams of cadmium oxide-boric oxide [11] and boric oxide-silicon dioxide [16] suggest that there are no solid solutions in either of these. In addition Van Vlack [19] points out that, in close packed crystal structures, there can be extensive solid solution if the size of the host and substitutional ions do not differ by more than 15%, but that this limitation may be relaxed if the structures are not close packed. In addition, solid solution is limited if the host and substitution atoms have different valency, or for compounds having different structures.

Van Vlack [20] gives the ionic radii for six-fold coordination as Cd^{2+} 1.03 Å, B^{3+} 0.25 Å and Si^{4+} 0.41 Å; hence the three ions have widely different radii. In addition, the three ions have different valencies and the three oxides different structures; thus it can be seen that the conditions are not favourable for the formation of solid solutions.

A noticeable aspect of this work is that $2\text{CdO}.\text{B}_2\text{O}_3-2\text{CdO}.\text{SiO}_2$ is a stable tie line and the photoelectric compositions lie near to this. The optimized composition varies slightly from this line, but this is unimportant for the best composition [8], where the deviation from the tie corresponds to the addition of 1.8 wt% $\text{CdO}.\text{SiO}_2$, while for the second best composition this corresponds to 0.1 wt% $\text{CdO}.\text{SiO}_2$. These quantities would be very difficult to observe in the electron microscope, and impossible to detect using X-ray powder techniques. Thus, the diphasic glass that has been reported in this region [7] could be $2\text{CdO}.\text{B}_2\text{O}_3$ and $2\text{CdO}.\text{SiO}_2$. Of course, within the individual glass phases it is not known whether they are homogeneous; but if they are, then both of these are equally rich in CdO, and the suggestion [5] that the good photoconductive properties are related to a CdO-rich phase cannot be correct. Their other suggestion that there is an SiO_2 -rich phase acting as a phase boundary insulator may be correct.

Obviously the structure of the glass is important, but comparison of the subsolidus phases may give useful information on this. The crystal structure of $2\text{CdO}.\text{B}_2\text{O}_3$ has not been determined, but it has been shown that it is isomorphous with triclinic $2\text{MgO}.\text{B}_2\text{O}_3$ [13]; the structure of the latter has been shown to consist of MgO_6 octahedra sharing edges [21] to form infinitely long ribbons of breadth and thickness four and one octahedra, respectively. Calculations using the atomic parameters of $2\text{MgO}.\text{B}_2\text{O}_3$ [21] with the cell parameters of $2\text{CdO}.\text{B}_2\text{O}_3$ [13] indicate that the

closest distances of approach of the cadmium ions are in the range 3.37 to 3.48 Å, with an average of 3.44 Å. (As crystalline order is destroyed in the glass, the average is probably a more useful criterion). Similarly in the case of 2CdO.SiO₂ [14] the CdO₆ octahedra again share edges, but form a three-dimensional network; the closest distances of the cadmium are in the range 3.36 to 3.47 Å, with average 3.41 Å. The average distances are very similar for the two compounds.

According to Goodenough [6] conduction occurs by overlap of the d orbitals or by interaction between a strongly polarizing cation and the oxygen p orbitals. Furthermore, he derived the empirical formulae to define whether overlap occurred. These are;

$$R_c(3d) = [3.05 - 0.03(Z - Z_{Zr}) - 0.04\Delta(J(J + 1))]$$

for the 3rd series and

$$R_c(4d) = [3.93 - 0.03(Z - Z_{Zr}) - 0.04\Delta(J(J + 1))]$$

for the 4d series. These formulae give a critical distance of 3.69 Å [5] for the overlap of the d orbitals, and for both 2CdO.B₂O₃ and 2CdO.SiO₂ the cadmium-cadmium distances are within this critical distance.

However, Goodenough [22] makes two important points; first that his formulae were meant to be applicable to partially-filled d shells, especially at the lighter end of the transition metal series, and not to filled 4d shells in cadmium. Also, that there is a second explanation which he feels is more logical, and is that there is overlap of cadmium 4d¹⁰ band and the oxygen 2p⁶ bands to produce a broad 4d-2p mixed band that supports mobile carriers. If this is the case, then the Cd-O distances are more important than the Cd-Cd distances. In the case of 2CdO.B₂O₃ there are twelve independent Cd-O distances in the range 2.11 to 2.49 Å; average 2.27 Å, while for 2CdO.SiO₂ the octahedra are more distorted and the range of Cd-O distances is 2.11 to 2.60 Å; average 2.37 Å, and it is possible that the larger Cd-O distance in 2CdO.SiO₂ may restrict the movement of carriers through a glassy phase of this composition.

However, there is another possible explanation; cadmium oxide is also composed of CdO₆ octahedra; in this case the faces are shared. It has been pointed out that it is non-stoichiometric and one obtains compositions with several hundredths of atomic per cent excess of metal. It is this defect

structure which causes it to be a good electrical conductor [23]. The fact that CdO₆ octahedra in cadmium oxide may contain defects raises the possibility as to whether the same effect may exist in the CdO₆ octahedra in glasses, in which case the high photoconductivity may be due to the electrons moving between defect sites.

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References

1. E. P. DENTON, H. RAWSON and J. E. STANWORTH, *Nature* **173** (1954) 1030.
2. Bh. V. JANAKIRAMA-RAO, *J. Amer. Ceram. Soc.* **48** (1965) 311.
3. K. W. HANSON, *J. Electrochem. Soc.* **112** (1965) 994.
4. T. N. KENNEDY and J. D. MACKENZIE, *Phys. Chem. Glass* **8** (1967) 169.
5. D. W. STRICKLER and R. ROY, *J. Mater. Sci.* **6** (1971) 200.
6. J. B. GOODENOUGH, "Magnetism and the Chemical Bond" (Wiley Interscience, New York, 1963).
7. V. ČÁSLAVSKÁ, D. W. STRICKLER, D. GIBBON and R. ROY, *J. Mater. Sci.* **3** (1969) 154.
8. V. ČÁSLAVSKÁ, D. W. STRICKLER and R. ROY, *J. Amer. Ceram. Soc.* **52** (1926) 19.
9. C. MAZETTI and F. de CARLI, *Gazz. Chim. ital.* **56** (1926) 19.
10. Th. P. J. BOLDEN and F. A. KRÖGER, *Physica* **13** (1947) 216.
11. E. C. SUBBARAO and F. A. HUMMEL, *J. Electrochem. Soc.* **103** (1956) 29.
12. P. B. HART and E. G. STEWARD, *J. Inorg. Nucl. Chem.* **24** (1962) 633.
13. W. D. HAND and J. KROGH-MOE, *J. Amer. Ceram. Soc.* **45** (1962) 197.
14. M. IHARA and J. KROGH-MOE, *Acta Cryst.* **20** (1966) 132.
15. L. S. DENT GLASSER and F. P. GLASSER, *Inorg. Chem.* **3** (1964) 1228.
16. T. J. ROCKETT and W. R. FOSTER, *J. Amer. Ceram. Soc.* **48** (1965) 75.
17. F. C. KRACEK, G. W. MOREY and H. E. MERWIN, *Amer. J. Sci.* **35A** (1938) 143.
18. S. V. BERGER, *Acta Chem. Scand.* **7** (1953) 611.
19. L. H. VAN VLACK, "Physical Ceramics for Engineers" (Addison-Wesley Publishing Co. Inc., Reading, Mass., 1964) p. 52.
20. *Idem, ibid.* p. 302.
21. S. BLOCK, G. BURLEY, A. PERLOFF and R. D. MASON, Jr., *J. Res. Nat. Bur. Stand.* **62** (1959) 95.
22. J. B. GOODENOUGH, private communication (1977).
23. Z. M. JARZEBSKI, "Oxide Semiconductors" (Pergamon Press, Oxford, 1973) p. 239.

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