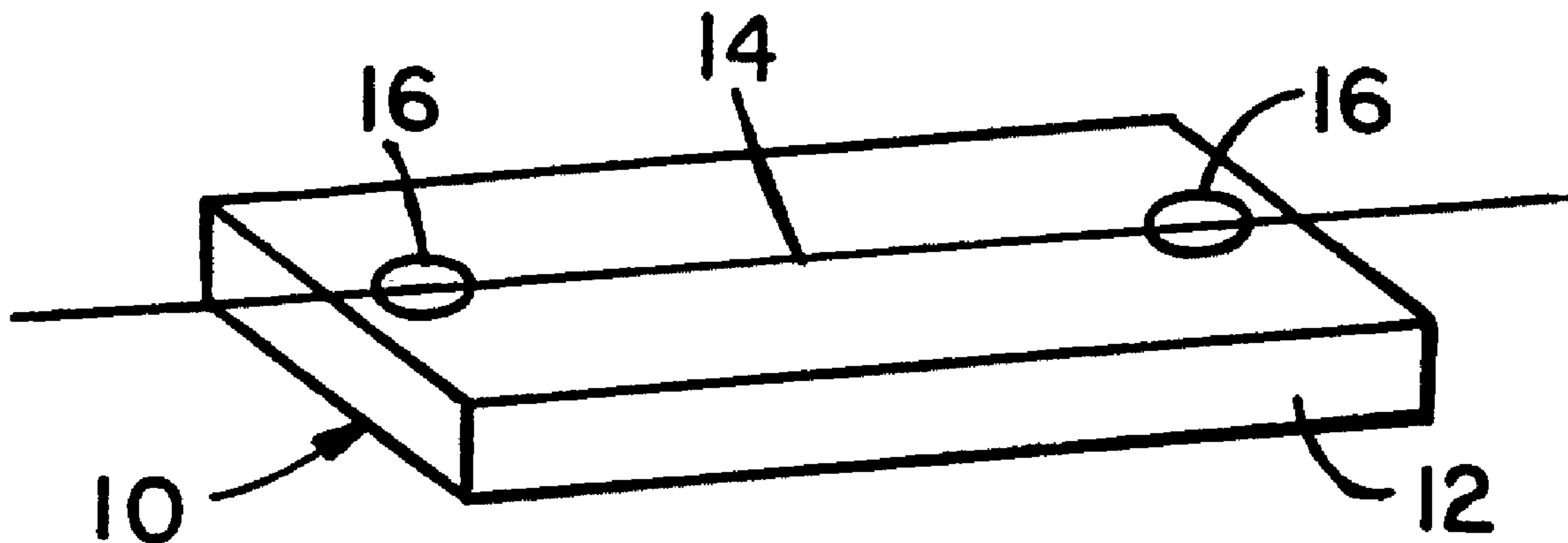




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 (54) Title: FUSION SEALED ARTICLE AND METHOD



(57) Abrégé/Abstract:

A telecommunication device (10) that comprises a low-expansion substrate (12), a low-expansion optical component such as an optical fiber (14) and a fusion seal (16) that maintains the substrate and the optical component in intimate contact, the fusion seal being a copper aluminosilicate glass. Also disclosed are copper aluminosilicate sealing glasses and a method of producing such glasses.

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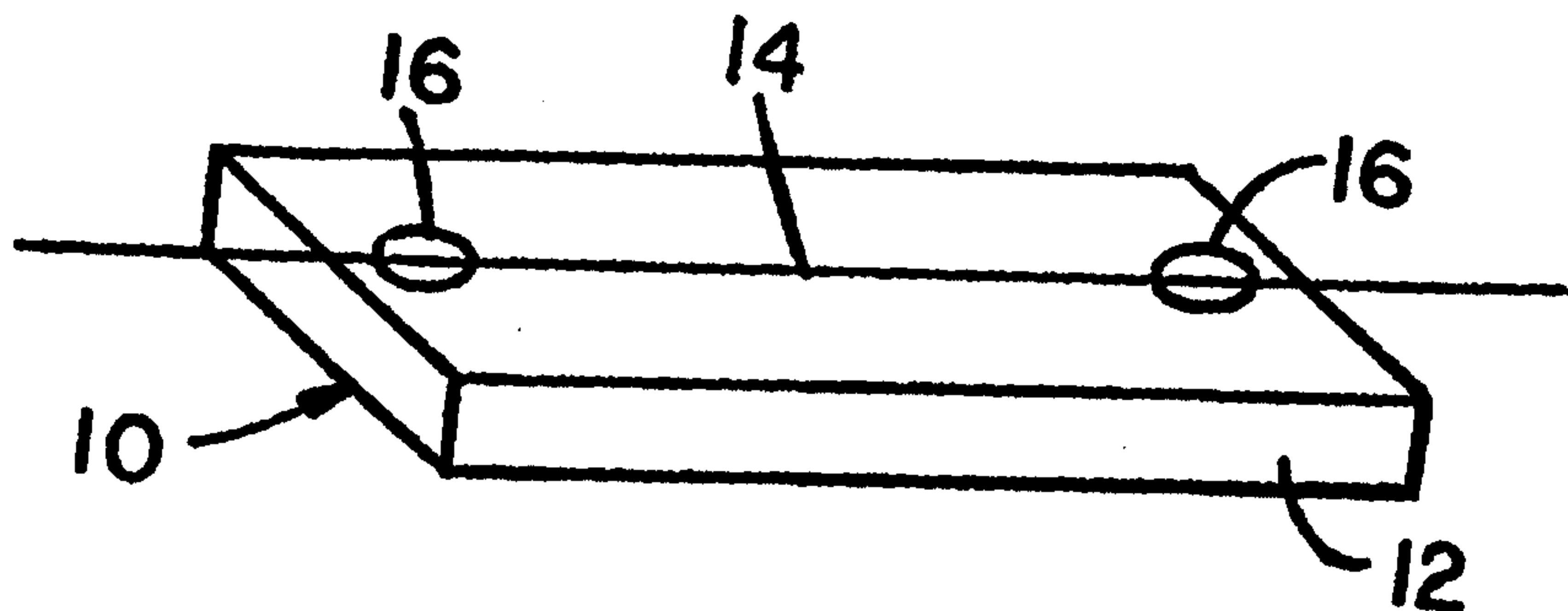
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A telecommunication device (10) that comprises a low-expansion substrate (12), a low-expansion optical component such as an optical fiber (14) and a fusion seal (16) that maintains the substrate and the optical component in intimate contact, the fusion seal being a copper aluminosilicate glass. Also disclosed are copper aluminosilicate sealing glasses and a method of producing such glasses.



FUSION SEALED ARTICLE AND METHOD

5 This application claims the benefit of U. S. Provisional Application,
Serial Number 60/107,379, filed November 6, 1998 entitled FUSION SEALED
ARTICLE AND METHOD, by Dianna M. Young.

RELATED APPLICATIONS

10 Provisional Application No. 60/107,381, filed November 6, 1998, entitled
ATHERMAL OPTICAL WAVEGUIDE GRATING DEVICES, by Dana
Bookbinder et al.

FIELD OF THE INVENTION

15 Telecommunication article having a seal produced with a copper
aluminosilicate sealing glass, and method of producing the glass.

BACKGROUND OF THE INVENTION

20 It is known that sealing glasses, composed essentially of oxides of
copper, aluminum and silicon, may have coefficients of thermal expansion
(CTEs) less than $10 \times 10^{-7} / ^\circ\text{C}$. over a broad temperature range. This property
has led to such sealing glasses being proposed for joining fused silica, quartz
and low-expansion glass-ceramic, structural components. In particular, such

glasses have been proposed for use in constructing large mirrors such as used in astronomy studies.

The recent burst of technological advances in telecommunication devices has caused a renewed interest in copper aluminosilicate sealing glasses. In particular, a critical need has arisen for a stable sealing material to use in joining low-expansion components to form telecommunication devices. One such application involves sealing a silica fiber to a low-expansion substrate, such as a glass-ceramic, to form a mechanically stable device.

Commercially available, copper aluminosilicate sealing glasses have been found to be of marginal utility in meeting the need. They form a rigid, vitreous seal, but have certain properties that require improvement.

One problem with known glasses is their tendency to have softening points in excess of 900° C. This requires high sealing temperatures that are difficult to control. Further, the glasses require melting temperatures over about 1500° C., again a condition not easily maintained. Finally, the glasses have expansion coefficients that tend to be higher than desired for telecommunication devices.

Accordingly, studies were undertaken to develop improved sealing glasses for use in telecommunication devices. A particular facet of these studies was development of copper aluminosilicate sealing glasses having low softening points and coefficients of thermal expansion. The present invention is primarily directed to improved, sealing glasses developed during these studies, and to methods of producing such improved sealing glasses.

25

SUMMARY OF THE INVENTION

The invention resides in part in a telecommunications device comprising a substrate having a low positive, or negative, thermal expansion coefficient, a low-expansion optical component, and a fusion seal that maintains the substrate and the optical components in intimate contact, the fusion seal being a copper alumino-silicate glass that has a coefficient of thermal expansion (CTE) less than $20 \times 10^{-7} / ^\circ\text{C}$. (25-500° C.) and that consists essentially of, as

30

calculated in weight percent on an oxide basis, 33-70% SiO₂, 10-35% Al₂O₃, 10-40% Cu₂O, 0-10% B₂O₃, 33-70% SiO₂+B₂O₃, 10-35% Al₂O₃+B₂O₃ and 0-10% P₂O₅, the copper oxide being essentially completely in the cuprous state.

5 The invention also resides in a method of producing a copper aluminosilicate glass in which the copper is essentially present in the cuprous state, the method comprising mixing a glass batch containing cuprous oxides as a source of copper, melting the glass batch while maintaining the melt in a mildly oxidized condition during melting to avoid formation of copper particles.

10 The invention further comprehends a copper aluminosilicate sealing glass that has a softening point less than 900° C., that has a CTE less than about $20 \times 10^{-7} / ^\circ\text{C}$., that has a composition consisting essentially of, as calculated in weight percent on an oxide basis, 33-70 SiO₂, 10-35% Al₂O₃, 10-40% Cu₂O, 0-10% P₂O₅, 0-10% B₂O₃, 33-70% SiO₂+B₂O₃, and 10-35% Al₂O₃+B₂O₃, the copper oxide being essentially completely in the cuprous
15 state.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings,
20 FIGURE 1 is a schematic drawing illustrating a simple, telecommunication device in accordance with the invention.

FIGURE 2 is a graphical representation of the glass-forming area of the ternary, Cu₂O-Al₂O₃-SiO₂ system at a melting temperature of 1500° C.

25 FIGURE 3 is a graphical representation showing the mismatch between a glass of the present invention and fused silica.

BRIEF DESCRIPTION OF THE INVENTION

30 The present invention arose from a search for copper aluminosilicate sealing glasses that would be more effective, and/or advantageous, in maintaining an optical component in intimate contact with a supporting substrate. More particularly, the article that required the improved sealing

glass was an optical waveguide grating device as described in related application S.N. _____. However, the invention finds broader application in joining optical components where a low-expansion, sealing glass is required. These include optical waveguide fibers and planar components used in telecommunication equipment.

FIGURE 1 is a schematic, side view of a simple, optical waveguide device 10 illustrating the article of the invention. Device 10 comprises a substrate member 12 that supports an optical fiber 14, and glass members 16 that secure fiber 14 to substrate 12. Glass members 16 may form a fusion seal between fiber 14 and substrate 12. Alternatively, they may be applied over fiber 14, and sealed to substrate 12, to securely maintain fiber 14 in intimate contact with substrate 12.

Optical communication occurs entirely through fiber 14. However, successful communication may depend on fiber 14 being held in a fixed position, and/or under a degree of tension. Accordingly, substrate 12 should have a coefficient of thermal expansion no greater than that of the fiber, and preferably lower.

Where a degree of tension is desired, as in an athermal device, the substrate must have a lower CTE, and may have a negative value. This permits the substrate to contract to a lesser degree, or even to expand, on cooling from the glass sealing temperature. This creates a degree of tension in fiber 14.

FIGURE 2 is a graphical representation of the glass-forming region at 1500° C. for the ternary system CuO-Al₂O₃-SiO₂. In the graph, the bottom line represents CuO content, the left hand side represents SiO₂ content, and the right hand side represents Al₂O₃ content. The apex represents 100 cation percent SiO₂. The experimental melts, upon which the graphical representation is based, were batched with CuO. However, the same compositions batched with Cu₂O should occupy the same region as explained later.

Within the compositional area outlined in FIGURE 2, either B₂O₃ or P₂O₅ may be substituted for either Al₂O₃ or SiO₂. The substitution may be in an

amount up to about 10% by weight. Preferably, the substitution is in an amount of 1-4%.

Such substitution lowers the annealing and softening points of a glass. It also suppresses a tendency for the glass to devitrify. Minor additions of either alkali metal oxides (R_2O) or alkaline earth metal oxides (RO), in place of copper oxide, also tends to soften the glass.

The present copper aluminosilicate sealing glasses consist essentially of, as calculated on an oxide basis in weight percent,

SiO_2	33-70
Al_2O_3	10-35
Cu_2O	10-40
B_2O_3	0-10
P_2O_5	0-10
R_2O	0-6
RO	0-6
$SiO_2+B_2O_3$	33-70
$Al_2O_3+B_2O_3$	10-35
Cu_2O+R_2O+RO	10-40

The glasses of the present invention exhibit softening points below $900^\circ C$. Preferred glasses will have softening points on the order of $800^\circ C$. and not over $850^\circ C$. This is in contrast to previously available commercial glasses having softening points substantially above $900^\circ C$. Thus, a glass currently available has a softening point of $915^\circ C$.

The glasses will have CTEs below $20 \times 10^{-7}/^\circ C$. over the temperature range of $25-500^\circ C$. Generally, these values are below $15 \times 10^{-7}/^\circ C$., and preferred glasses are below $10 \times 10^{-7}/^\circ C$. The glasses will melt and pour at temperatures on the order of $1500^\circ C$. These properties are optimized in a family of preferred compositions, again in weight percent on a calculated oxide basis, that consist essentially of,

SiO_2	43-50
Al_2O_3	17-23
Cu_2O	29-32
B_2O_3 or	1-4
P_2O_5	

The redox chemistry of the present copper aluminosilicate glasses is rather complicated. Thus, at high temperatures, the copper source is reduced to the lower, oxidation state of copper, that is, the Cu^+ , or cuprous, state. This occurs regardless of the oxidation state of the copper source in the parent glass batch. EPR and analytical studies confirm that copper exists mainly in the cuprous state in the present glasses.

My studies have consistently shown that glasses batched with Cu_2O provide the lowest, possible expansion coefficients over a wide temperature range. They also provide the lowest softening points. However, it has been found that, when Cu_2O is used as a source of copper in a glass batch, copper metal particles tend to form as a precipitate in the glass.

A feature of the present invention is based on the discovery that the formation of copper particles can be avoided. This involves including a small amount of a mild oxidizing agent, such as a nitrate, or a sulfate, in the batch from which the glass is melted. This provides a mildly oxidizing condition in the melt that is sufficient to avoid appreciable reduction to, and precipitation of, copper metal. At the same time, there appears to be no effect on other properties, in particular, the low softening point and expansion coefficient.

No more than about 5% by weight, and preferably no more than about 2%, of a metal nitrate or sulfate is included in the glass batch. Preferably, a sulfate of copper, copper nitrate, or aluminum nitrate, is used, such as up to 5 weight percent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Also, other sources, such as NH_4NO_3 and most nitrates and/or sulfates of transition metals, may be employed.

The copper aluminosilicate glasses just described may be used in various forms in telecommunication devices. Thus, they may be drawn as cane, tubing or fiber for packaging purposes. They may also be pulverized to form a glass sealing frit for use in conventional manner.

The invention is further described with respect to specific embodiments. TABLE I shows several compositions, together with CTEs and softening points, that illustrate the invention. The compositions are shown in weight percent.

TABLE I

Oxide (wt. %)	1	2	3	4	5	6	7	8	9
Cu₂O	31.2	30.3	31.1	30.5	30.5	30.4	31.2	21.8	39.9
Al₂O₃	17.7	17.9	17.7	20.2	19.8	17.7	17.7	18.0	17.6
B₂O₃	2.9	2.9	2.9	-	2.9	2.9	2.9	3.0	2.9
P₂O₅	-	-	-	3.0	-	-	-	-	-
SiO₂	48.0	48.7	48.2	46.3	46.9	47.9	48.0	57.2	39.6
Co₃O₄	-	-	-	-	-	1.0	-	-	-
CTE (x10⁻⁷)	5.2	10.0	6.5	6.6	7.0	8.7	7.4	7.7	11.2
Soft. Pt.	830	747	802	795	795	-	795	866	785

Composition 1 is presently preferred because of its low CTE. This composition, and compositions 3-7 illustrate embodiments within the preferred composition ranges and having CTEs below $10 \times 10^{-7}/^{\circ}\text{C}$. Compositions 8 and 9 illustrate compositions within the broad ranges. They demonstrate low and high Cu₂O contents, respectively, and, conversely, high and low contents of SiO₂.

TABLE II shows the batches melted to produce the glasses having the compositions shown in TABLE I. In this case, the materials are in parts by weight.

TABLE II

Batch (grams)	1	2	3	4	5	6	7	8	9
Cu₂O	92.0	-	156.0	85.8	92.0	153.0	91.9	217	389
CuO	-	167.0	-	-	-	-	-	-	-
Al₂O₃	51.8	85.7	86.3	56.2	44.4	86.3	51.8	177	169
AlF₃	-	-	-	-	12.0	-	-	-	-
B₂O₃	8.5	14.2	14.2	-	8.5	14.2	8.54	29.2	27.8
Al(PO₃)₃	-	-	-	21.3	-	-	-	-	-
SiO₂	140.0	234.0	234.0	129.0	140.0	234.0	140.0	559.0	380.0
CuSO₄·5H₂O	6.7	-	-	5.9	6.0	-	-	10.3	19.6
Cu(NO₃)·3H₂O	-	-	-	-	-	-	6.3	-	-
NH₄NO₃	-	-	5.0	-	-	-	-	-	-
Co(NO₃)₂	-	-	-	-	-	11.7	-	-	-

Compositions 1 and 2 illustrate the effect of Cu₂O vs. CuO as batch ingredients. The compositions are essentially the same, but the CTE of the glass from batch 2 is double that of the glass from composition 1. This indicates the effectiveness of using cuprous oxide as a batch ingredient.

The batches were formulated and mixed in conventional manner. Each batch was placed in a silica crucible, and the crucible placed in an electric furnace operating at about 1500° C. At the end of a four hour melting period, the melts were poured into molds to provide test pieces for chemical and physical analyses.

FIGURE 3 is a graphical representation of an inventive feature of particular interest. Temperature, in ° C., is plotted on the horizontal axis. Expansion mismatch vs. fused silica, in parts per million (ppm), is plotted on the vertical axis. The central, horizontal line represents zero mismatch over the temperature range 0-600° C.

The curve shown in FIGURE 3 is based on measurements made on an inverse sandwich seal between fused silica and a sealing frit having the composition of Example 1 in TABLE I. The data plotted were measured as the seal was cooled from a sealing temperature of about 550° C. to ambient. The mismatch between the present glass and fused silica is consistently negative.

The degree of mismatch that can be tolerated in a seal is dependent on size and geometry of the seal and of the components being sealed. For relatively small seals, such as contemplated here, a mismatch up to about 400 ppm between a commercial sealing glass and fused silica has been deemed tolerable.

It is a feature of the present invention that a mismatch in the range of 100-200 ppm can be obtained. At room temperature, mismatch is below 100 ppm, a particularly favorable condition. This is illustrated in the preferred example of FIGURE 3. There, the maximum mismatch is on the order of 150 ppm.

WE CLAIM:

1. A telecommunication device comprising a low-expansion substrate, having a low positive, or negative, thermal expansion coefficient, a low-
5 expansion optical component, and a fusion seal that maintains the substrate and optical component in intimate contact, the fusion seal being a copper aluminosilicate glass that has a coefficient of thermal expansion (CTE) less than $20 \times 10^{-7} / ^\circ\text{C}$. (25-500° C.), and that consists essentially of, as calculated in weight percent on an oxide basis, 33-70% SiO₂, 10-35% Al₂O₃, 10-40% Cu₂O,
10 0-10% B₂O₃, 33-70% SiO₂+B₂O₃, 10-35% Al₂O₃+B₂O₃ and 0-10% P₂O₅, the copper oxide being essentially completely in the cuprous state.
2. A telecommunication device in accordance with claim 1, wherein the copper aluminosilicate glass has a softening point less than 900° C.
15
3. A telecommunication device in accordance with claim 1, wherein the composition of the copper aluminosilicate glass, as calculated in weight percent on an oxide basis, consists essentially of 43-50% SiO₂, 17-23% Al₂O₃, 29-32% Cu₂O, 1-4% B₂O₃.
20
4. A telecommunication device in accordance with claim 1, which comprises a Bragg grating.
5. A telecommunication device in accordance with claim 1, in which the
25 optical component is a waveguide fiber.
6. A telecommunication article in accordance with claim 1, in which the substrate is a low-expansion glass-ceramic or a fused silica.
- 30 7. A telecommunication device in accordance with claim 1, in which the substrate is a glass-ceramic with a negative coefficient of thermal expansion.

- 5 8. A method of producing a copper aluminosilicate glass with the copper essentially present in the cuprous state which comprises mixing a glass batch containing cuprous oxide as the source of copper, melting the batch, and maintaining the melt in a mildly oxidized condition to avoid formation of copper particles.
9. A method in accordance with claim 8, which comprises maintaining the melt in a mildly oxidized condition by including a mildly oxidizing agent in the glass batch.
- 10 10. A method in accordance with claim 9, which comprises mixing a glass batch containing a mildly oxidizing agent selected from the group consisting of nitrates and sulfates.
- 15 11. A method in accordance with claim 9, which comprises mixing a glass batch containing up to about 5% by weight of a mildly oxidizing agent.
12. A method in accordance with claim 11, wherein the glass batch contains up to about 2% by weight of the mildly oxidizing agent.
- 20 13. A method in accordance with claim 8, which comprises melting the batch at a temperature not over about 1500° C.
- 25 14. A copper aluminosilicate glass that has a softening point less than 900° C., that has a CTE less than about $20 \times 10^{-7} / ^\circ\text{C}$., that can be melted and delivered at a temperature not over about 1500° C., and that has a composition, as calculated in weight percent on an oxide basis, consisting essentially of 33-70% SiO₂, 10-35% Al₂O₃, 10-40% Cu₂O, 0-10% B₂O₃, 0-10% P₂O₅, 0-6% R₂O, 0-6% RO, 33-70% SiO₂+B₂O₃, 10-35% Al₂O₃+B₂O₃ and 10-30 40% Cu₂O+R₂O+RO, the copper oxide being essentially completely in the cuprous state.

15. A copper aluminosilicate glass in accordance with claim 14 having a composition consisting essentially of 43-50% SiO₂, 17-23% Al₂O₃, 29-32% Cu₂O, 1-4% B₂O₃.

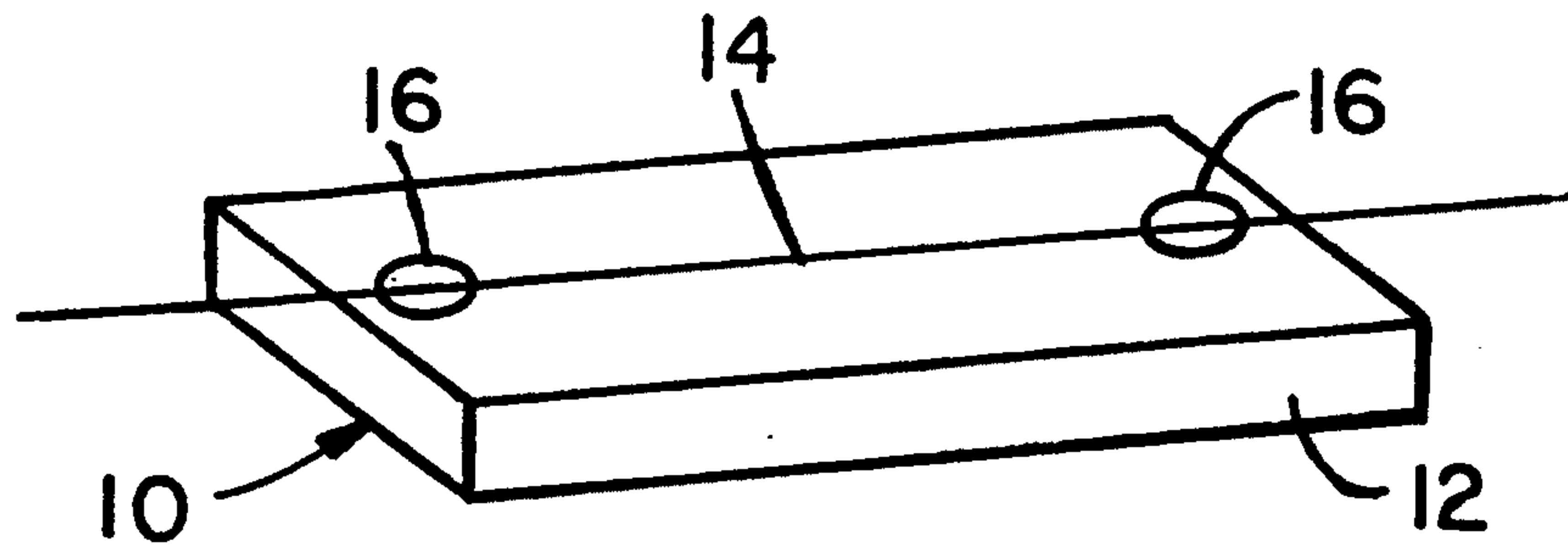


Fig. 1

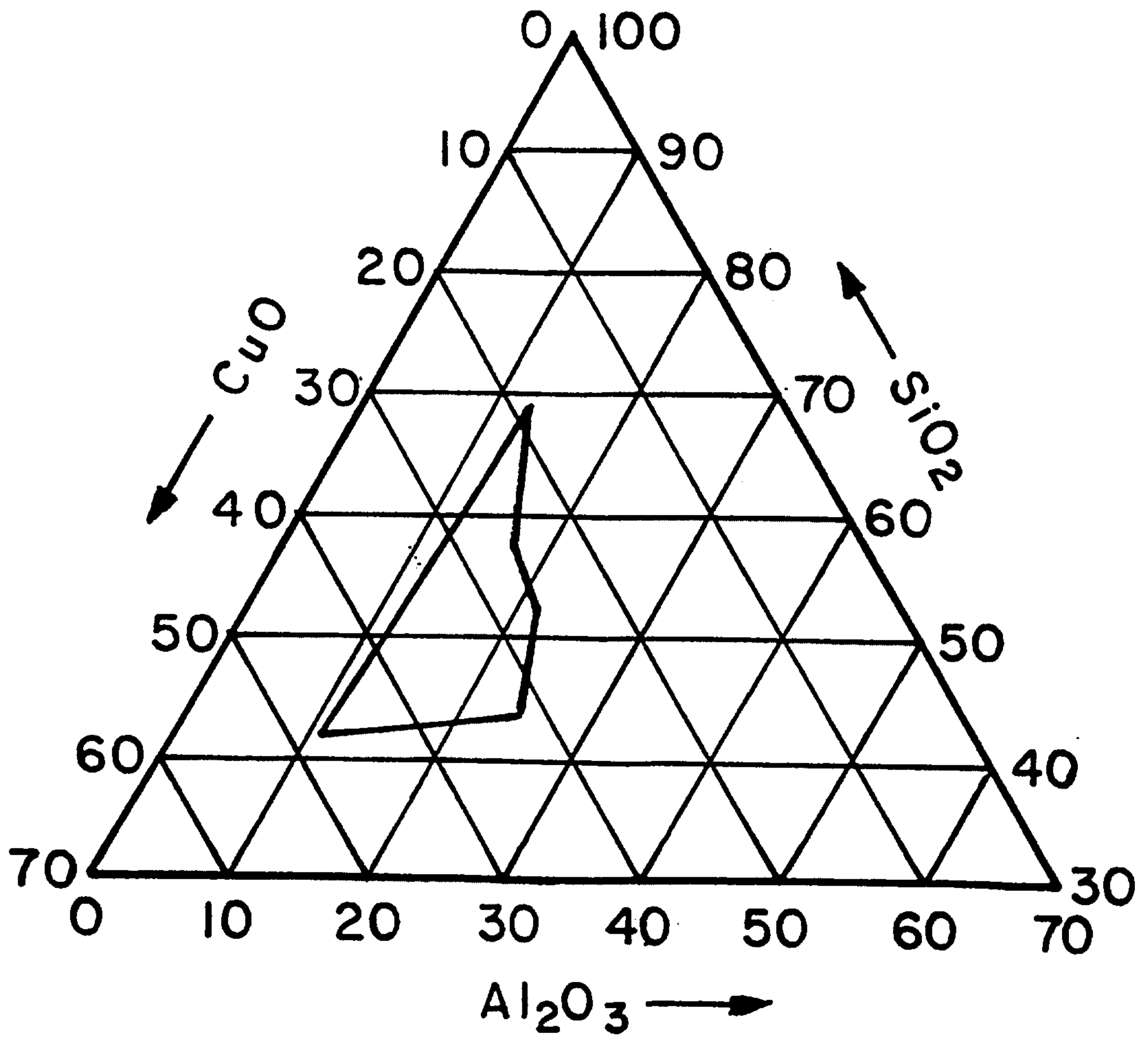


Fig. 2

Fig. 3

