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13. ABSTRACT *(Maximum 200 words)*

Two different methods were used to prepare tough glass-ceramics containing ZrO_2. One was to melt ZrO_2-containing Li_2O-Al_2O_3-SiO_2 glasses and transform them by controlled crystallization. The other was to sinter BaO-SiO_2-Al_2O_3 glass powder together with ZrO_2 powder. In both materials, some toughness improvement by the transformation of zirconia during fracture was observed. However, unexpectedly, the greater toughness improvement was realized when the zirconia particles in the glass-ceramics were transformed prior to the fracture by cooling to a lower temperature, e.g., liquid nitrogen temperature. This drastic increase of the fracture toughness was attributed to the deflection of the propagating crack by the large stress fields around the transformed (monoclinic) zirconia. The examination of the fracture surface demonstrated clearly that the crack deflection is taking place in the specimen with transformed zirconia.

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HIGH-TOUGHNESS GLASS-CERAMICS

FINAL REPORT

MINORU TOMOZAWA

August 31, 1994

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER DAAL03-91-G-0211

RENSSELAER POLYTECHNIC INSTITUTE
TROY, NY 12180-3590

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STATEMENT OF THE PROBLEMS STUDIED

Glasses and ceramics have many desirable characteristics such as light weight and refractoriness. But in general they lack toughness, or the ability to resist crack propagation. Tougher glass and ceramics are desired in many applications. Addition of ZrO_2 at high temperature is one of the effective ways to increase the toughness of glasses and ceramics. A high temperature form of zirconia, tetragonal zirconia, transforms upon cooling at ~1000°C to monoclinic zirconia and expands. When ZrO_2 powder is dispersed in a glass or ceramic matrix, this transformation is shifted to lower temperature or suppressed until the time of fracture. Transformation during fracture reduces the crack tip tensile stress, thus making the crack propagation difficult. This mechanism of toughening, called transformation toughening, has been applied to a variety of different ceramics. Application of this toughening process to glass-ceramics has been investigated in this research program. Glass-ceramics with zirconia have been prepared by two different methods: (i) melting of glass containing zirconia and crystallizing the glass by controlled heat-treatment, (ii) glass powder is sintered together with zirconia powder and crystallized. The former is simpler in operation, but it usually requires a high temperature for glass melting, especially when the incorporation of a large amount of ZrO_2 is desired. In the latter, a larger quantity of ZrO_2 can be incorporated more easily but the process is more complicated and the product usually contains pores.

SUMMARY OF THE MOST IMPORTANT RESULTS

I. Fracture Toughness of ZrO_2-containing Glass-Ceramics

(A) Melting method.

Up to 15 wt% ZrO_2 was added to the Li_2O-Al_2O_3-SiO_2 system which, upon heat-treatment, produced β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) phase. While the fracture toughness was observed to increase with ZrO_2 addition, primarily because of the large thermal expansion anisotropy of the β-eucryptite phase, extensive spontaneous cracking occurred when the grain size of this phase becomes larger than ~1 μm.

(B) Sintering method.

A BaO-SiO_2-Al_2O_3 glass which produced the best sintering characteristic was melted and pulverized. To this glass powder, various amounts of 10 vol% CeO_2-stabilized tetragonal ZrO_2 powder were added and sintered. The fracture toughness increase by more than 100% was possible by choosing the grain size of tetragonal zirconia powder. Even greater increase of fracture toughness was realized by transforming tetragonal zirconia to monoclinic zirconia by cooling the specimen to liquid nitrogen temperature prior to the mechanical testing at room temperature. Selected fracture toughness results are shown below.

	fracture toughness($MPa\sqrt{m}$) at room temperature
(a) BaO-SiO_2-Al_2O_3 glass-ceramics	0.9 ± 0.1
(b) BaO-SiO_2-Al_2O_3 + 10 vol% ZrO_2	1.8 ± 0.3
(c) sample (b), after cooling to liq. N_2	3.0 ± 0.6

Apparently, several different mechanism are operating in

ZrO_2-containing glass-ceramics. The following toughness processes appear to be involved.

(i) ZrO_2 transformation toughening.

This involves the stress-induced transformation of tetragonal ZrO_2 to monoclinic ZrO_2. This was the originally intended mechanism.

(ii) residual stress toughening.

Thermal expansion mismatch of two phases or two directions of single phases produces residual stress. This can cause toughening in some $Li_2O-Al_2O_3-SiO_2$ systems.

(iii) crack deflection by inclusion.

When tetragonal ZrO_2 transforms into monoclinic ZrO_2 in a glass-ceramic matrix, an extremely large stress is produced around the transformed particle. This causes crack deflection and leads to toughening.

Of particular interest in this research is the greater toughness improvement realized when the zirconia particles in the glass-ceramics transformed <u>prior to</u> the fracture. The accompanying figures demonstrate the crack deflection mechanism. The cooled specimens with transformed (monoclinic) zirconia exhibit tortuous path for cracks. For example, figure (a) and (b), which show the fracture surfaces, reveal a rougher surface for sample cooled to liquid nitrogen temperature. Correspondingly, figure (c) and (d), which show zirconia on the fracture surface, reveal more zirconia after cooling, even though the zirconia content remains unchanged, indicating that the cracks are deflected towards zirconia particles.

II. Crystallization of Lithium-Disilicate Glass

In the course of crystallization study of glasses, an interesting phenomenon was observed. Usually, lithium disilicate glasses crystallize into lithium silicate, $Li_2O \cdot 2SiO_2$ without changing composition. Some reported that metastable lithium metasilicate crystals ($Li_2O \cdot SiO_2$) precipitated first and then disappeared by a longer heat-treatment. It was discovered that the lithium metasilicate crystal precipitated from lithium silicate glasses predominantly when the glass was heat-treated in a $LiNO_3$ melt near the glass transition temperature. Apparently the lithium oxide is incorporated into the glass from the $LiNO_3$ melt at the treatment temperature. This is contrary to the commonly accepted notion that at the glass transition temperature, only Li is mobile but not oxygen.

List of Publications

1. "Sintering and Crystallization of BaO-SiO_2 System Glass-ZrO_2 Powder Mixtures," Srinivasan Sridharan and Minoru Tomozawa, Ceramic Tans., **30**, 363 (1993).

2. "Effect of Various Oxide Additives on Sintering of BaO-SiO_2 System Glass-Ceramics," S. Sridharan and M. Tomozawa, J. Mat. Sci. **27**, 6747 (1992).

3. "Glass-Ceramics as New Materials," Minoru Tomozawa and Richard D. Sarno, Chem. Express, **6**, 949 (1991).

4. "Toughening of Glass-Ceramics by both Transformable and Transformed Zirconia," S. Sridharan and M. Tomozawa, to appear in J. Non-Cryst. Solids.

5. "Crystallization of Lithium Metasilicate From Lithium Disilicate Glass," Jeffrey R. Jacquin and Minoru Tomozawa, to appear in J. Non-Cryst. Solids.

6. "Toughening of Sintered Glass-Ceramics by Zirconia," Srinivasan Sridharan, Ph.D. Thesis (1994).

7. "Crystallization of Lithium Metasilicate From Lithium Disilicate Glass," Jeffrey R. Jacquin, Master's Thesis (1994).

8. "Microstructure Development and Mechanical Properties of Lithium Aluminum Silicate-Zirconia Glass-Ceramics," Richard D. Sarno, Ph.D. Thesis (1994).

9. "Toughening Mechanisms for a Zriconia-Lithium Aluminosilicate Glass-Ceramics," Richard D. Sarno and Minoru Tomozawa, Submitted to J. Mat. Sci.

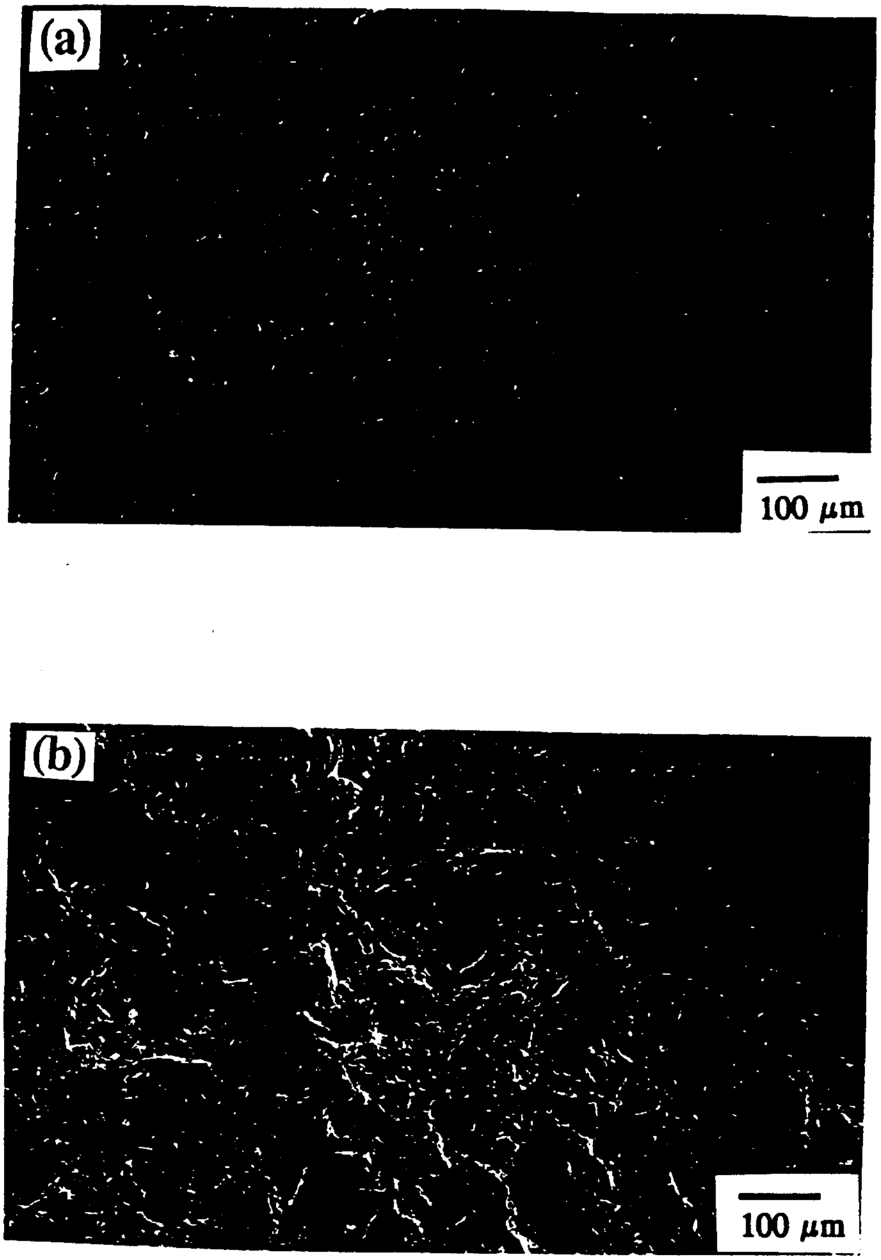
PARTICIPATING SCIENTIFIC PERSONNEL

Minoru Tomozawa, Principal Investigator, Professor of Materials Engineering.

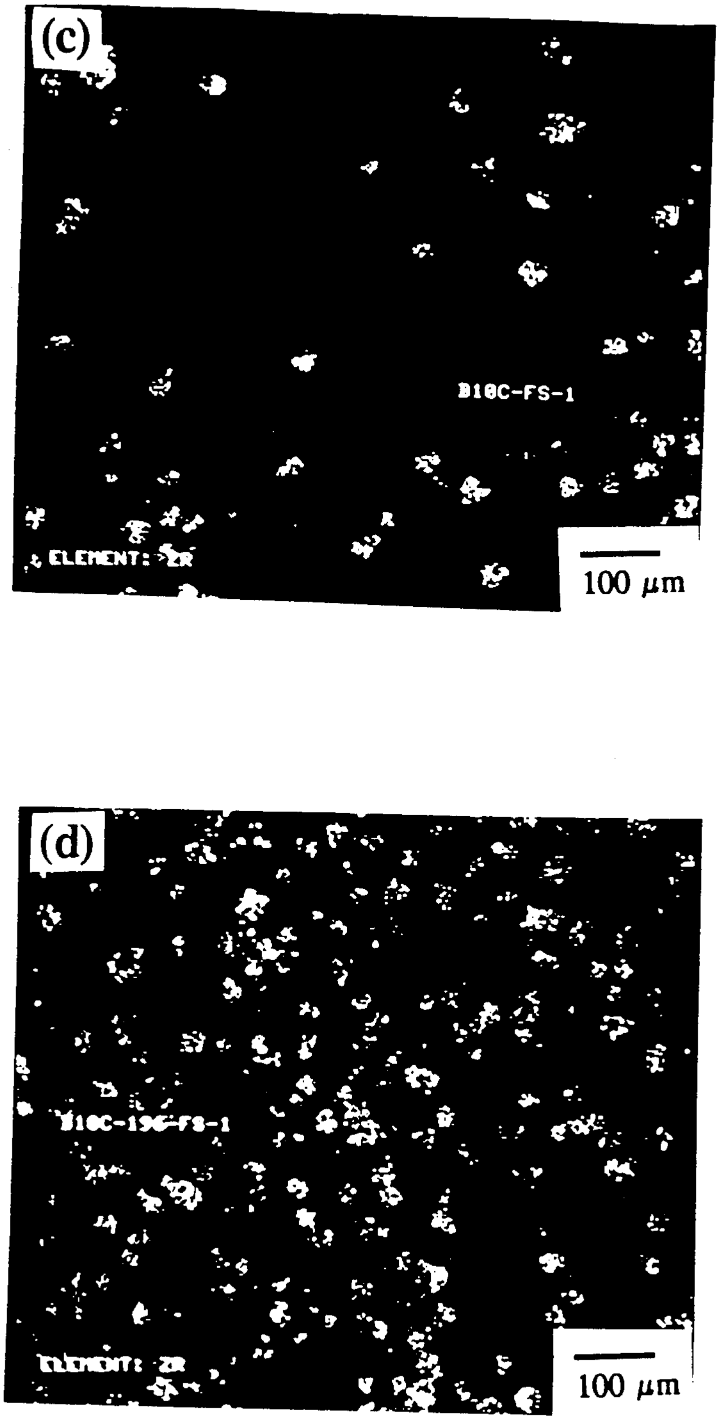
Richard D. Sarno, Research Assistant, earned Ph.D. in December, 1993.

Sridharan Srinivasan, Research Assistant, earned Ph.D. in December, 1993.

Jeffrey R. Jacquin, Research Assistant, earned Master's Degree, December, 1993.



Secondary electron image of the fracture surface.
(a) before cooling, (b) after cooling.



Energy dispersive x-ray mapping of Zr on the fracture surface.

(c) before cooling, (d) after cooling.