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CRYSTALLIZATION AND MICROSTRUCTURAL CONTROL OF FERROELECTRIC THIN-FILMS AND GLASS-CERAMICS

Interim Report for the Period March 1, 1992 to September 30, 1993

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13. ABSTRACT *(Maximum 200 words)*

Research on solution-derived ferroelectric thin-films and melt-derived ferroelectric glass-ceramics is being conducted in parallel with considerable overlap in the compositions studied and the evaluations of the crystallization behavior, microstructural development, and resulting properties. By establishing the similarities and differences between the two systems, techniques developed for one technology can then be applied to advance the other. The investigation is focusing on the $Pb(Zr_xTi_{1-x})O_3$-$Pb_5Ge_3O_{11}$ (PZT-PG) system. Compositions from this system combine the glass forming ability and low processing temperatures of PG with the excellent electrical properties of PZT. These compositions crystallize into multiple ferroelectric phases, and thus by controlling the ratios of these phases unique combinations of properties may be possible. The high PG compositions are being investigated for pyroelectric applications, while the high PZT compositions are of interest for piezoelectric applications. This program appears to be the first to investigate melt-derived PG-PZT compositions, crystallize multiple ferroelectric phases, and crystallize PZT from a glass. This research demonstrates the feasibility of developing piezoelectric glass-ceramics with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting, and indicates the potential of incorporation of these materials into low-fired multilayer packages as a sensors or actuators.

14. SUBJECT TERMS
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ABSTRACT

Research on solution-derived ferroelectric thin-films and melt-derived ferroelectric glass-ceramics is being conducted in parallel with considerable overlap in the compositions studied and the evaluations of the crystallization behavior, microstructural development, and resulting properties. By establishing the similarities and differences between the two systems, techniques developed for one technology can then be applied to advance the other. The investigation is focusing on the $Pb(Zr_xTi_{1-x})O_3$-$Pb_5Ge_3O_{11}$ (PZT-PG) system. Compositions from this system combine the glass forming ability and low processing temperatures of PG with the excellent electrical properties of PZT. These compositions crystallize into multiple ferroelectric phases, and thus by controlling the ratios of these phases unique combinations of properties may be possible. The high PG compositions are being investigated for pyroelectric applications, while the high PZT compositions are of interest for piezoelectric applications. This program appears to be the first to investigate melt-derived PG-PZT compositions, crystallize multiple ferroelectric phases, and crystallize PZT from a glass. This research demonstrates the feasibility of developing piezoelectric glass-ceramics with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting, and indicates the potential of incorporation of these materials into low-fired multilayer packages as a sensors or actuators.

I. INTRODUCTION

This report summarizes the activities carried out in the Colorado Center for Advanced Ceramics at the Colorado School of Mines from March 1, 1992 to September 30, 1993 on the ONR sponsored research program, "Crystallization and Microstructural Control of Ferroelectric Thin-Films and Glass-Ceramics." This research is supported by an ONR Young Investigator Award combined with an Augmentation Award for Science and Engineering Research Training (AASERT). Additional support for this project is being provided with funding from an NSF Presidential Young Investigator Award, and from the Colorado School of Mines through significant reduction of overhead charges, summer faculty support, and funding for equipment.

With the combined funding the research program was divided into the following four projects with at least one graduate student working on each project:

- Lead Germanate Based Ferroelectric Glass-Ceramics,
- Lead Germanate Based Ferroelectric Thin-Films,
- Lead Borosilicate Based Ferroelectric Glass-Ceramics, and
- Ferroelectric Thick-Films.

The first project was started in August 1991 with support of a graduate student from the base grant of the PYI Award from NSF. The other three projects were started in March 1992 with funding for three additional graduate students from the ONR support.

The overall scientific research goals of this program are summarized in the next section, followed by summaries of the specific objectives and results of each of the four projects listed above. Additional details of these projects are provided in the appendices. The plans for next years research are discussed in Section VII. Research facilities established from the ONR funding are described in Section VIII.

II. SCIENTIFIC RESEARCH GOALS

Ferroelectric thin-films and glass-ceramics both require the crystallization and microstructural development of the active phase from an amorphous material to produce the desired properties, and thus many similar technical questions exist in both systems. In this program, research on solution-derived ferroelectric thin-films and melt-derived ferroelectric glass-ceramics is being conducted in parallel with considerable overlap in the compositions studied and the evaluations of the crystallization behavior, microstructural development, and resulting properties. By establishing the similarities and differences between the two systems, techniques developed for one technology can then be applied to advance the other.

The investigation is focusing on the $PbTiO_3$ - $PbZrO_3$ - $Pb_5Ge_3O_{11}$ system. Compositions from this system combine the glass forming ability and low processing temperatures of $Pb_5Ge_3O_{11}$ (PG) with the excellent electrical properties of $PbTiO_3$ (PT) and $Pb(Zr_xTi_{1-x})O_3$ (PZT). These compositions crystallize into multiple ferroelectric phases, and thus by controlling the ratios of these phases unique combinations of properties may be possible. The high PG compositions are being investigated for pyroelectric applications, while the high PT and PZT compositions are of interest for piezoelectric applications.

The major objectives of the research are to:

- Develop an understanding of the relationships between the composition, crystallization, microstructure, and properties of solution-derived ferroelectric thin-films and melt-derived ferroelectric glass-ceramics.
- Model the compositional and property changes that occur as a function of crystallization to assist in the design of new compositions with enhanced performance.

- Determine the critical crystallite size and microstructure required to obtain ferroelectricity, piezoelectricity, etc.

- Identify compositional modification and processing techniques to lower heat treatment temperatures.

- Evaluate the effects of interactions of electrodes and substrates on the crystallization behavior of melt and sol-gel derived materials, and minimize interactions through compositional design.

- Establish the similarities and differences between the crystallization behavior and microstructural development of solution and melt-derived amorphous materials.

- Utilize the techniques used to control the crystallization behavior in glass-ceramics to improve the control of solution derived thin-film microstructures, and vice versa.

- Develop improved ferroelectric thin-films and glass-ceramics.

III. LEAD GERMANATE BASED FERROELECTRIC GLASS-CERAMICS

This project was started in August 1991 with support of a graduate student, I. A. Cornejo, from the base grant of the PYI Award from the National Science Foundation. Presentations on this research were given at the 1992 and 1993 Annual Meetings of the American Ceramic Society, and at the 8th International Meeting on Ferroelectricity. The results of this research are documented in Appendices 1 and 6-9, and summarized in the following paragraphs.

The crystallization behavior of amorphous compositions prepared from the $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) and $Pb_5Ge_3O_{11}$-$Pb(Zr_xTi_{1-x})O_3$ (PG-PZT) systems was investigated. Selected compositions were melted, quenched, and milled into powders. Some crystallization occurred depending on composition and quenching conditions. Pressed samples crystallize completely into multiple ferroelectric phases at 600°C (PG and PT, or PG and PZT), and densify to 93-99% of theoretical density at 700°C. This appears to be the first research to investigate melt-derived PG-PT and PG-PZT compositions, crystallize multiple ferroelectric phases, and crystallize PZT from a glass.

Densification of pressed PG based glass powders occurs at low temperatures (≈ 700°C), however the softening temperatures (≈ 340°C) of these glasses indicate the potential of densification at even lower temperatures. Processing conditions, especially the type of liquid used during milling, were found to control the densification behavior (see Appendix 9). Reaction with water was found to crystallize an unidentified phase in all compositions, which transforms to the desired ferroelectric phases during heat treatment. The rapid crystallization of the PG based glasses appears to limit the densification possible from glass softening without additional modification of the compositions. For example, partial substitution of silicon for germanium in PG to form $PbGe_{3-x}Si_xO_3$ has increased glass formability and lowered the densification temperatures possible, apparently because of the reduced rate of crystallization. Pressed $PbGe_2SiO_3$ glass powder densifies to 96% of theoretical density at 620°C. Additional modifications to process at even lower temperatures is planned for future research.

In addition to crystallizing multiple ferroelectric phases, the sizes of PG, PT, and PZT crystallites can be controlled from submicron to >10 μm depending on the heat treatment conditions. Ferroelectric hysteresis loops and electrical poling of these initial samples has been limited. A variety of processing methods and compositional modifications to improve the poling are currently under investigation. Crystallization of amorphous films can be controlled to produce c-axis orientation of the ferroelectric PG phase (see Appendix 5). Addition of $PbTiO_3$ or $PbZr_xTi_{1-x}O_3$ to PG results in decreased c-axis orientation of the PG crystallites in thick-film samples, however significantly enhanced orientation occurs in thin-film form (discussed in the next section). The high thermal expansion coefficient of PG (≈ 14 ppm/°C) has resulted in cracking of films on alumina substrates. The compatibility with higher thermal expansion substrates such as MgO is currently under investigation.

IV. LEAD GERMANATE BASED FERROELECTRIC THIN-FILMS

Solution-derived ferroelectric thin-films of compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ system are being investigated by S. M. Landin. As discussed above this system potentially combines the excellent electrical properties of $PbTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$ with the low processing temperatures of $Pb_5Ge_3O_{11}$. Compositions are being formulated through a solution process leading to both bulk powders and thin films. The densification behavior, microstructural development, and electrical properties relative to both composition and processing temperature are being studied. Presentations on this research were given at the 1993 Annual Meeting of the American Ceramic Society, and at the 8th International Meeting on Ferroelectricity. Appendix 2 provides additional details on this research.

Solution-derived powders with compositions $Pb_5Ge_3O_{11}$, $Pb_5Ge_3O_{11}$-$2PbTiO_3$ and $Pb_5Ge_3O_{11}$-$2PbZr_{0.5}Ti_{0.5}O_3$ were observed to form the 5-3 ferroelectric phase of PG between

550 and 600°C. In the PG-PT system, pyrochlore PT transforms to perovskite at approximately 600°C, while the pyrochlore PZT to perovskite transformation is observed at 650°C. PG thin films show rapid orientation of the c-axis which increases with increasing temperature. PG thin films on glass substrates with 59% c-axis orientation were achieved by heat treatment at 600°C, however above 650°C these films lose their crystallographic structure. C-axis orientation of 38% was observed in PG thin films on platinum electroded silicon substrates. This orientation increases to greater than 90% with the addition of PZT to form the PG-2PZT composition. Future research is needed to understand the mechanisms responsible for this dramatic increase in orientation with PZT addition.

V. LEAD BOROSILICATE BASED FERROELECTRIC GLASS-CERAMICS

A wide range of ferroelectric compositions in the $xPb(Zr_yTi_{1-y})O_3 \cdot zPbO \cdot wSiO_2 \cdot uB_2O_3$ system, where x=0.6 or 0.8, y=0 or 0.52, z=0-0.28, w=0-0.4, and u=0-0.4 are being investigated by B. Houng to develop an understanding of the critical crystallite size and microstructure required to achieve useful piezoelectric and pyroelectric properties in glass-ceramics. Presentations on this research were given at the 1993 Annual Meeting of the American Ceramic Society, and at the 8th International Meeting on Ferroelectricity. Appendix 3 provides additional details on this research.

PT or PZT ferroelectric phases crystallize with nonferroelectric residual glass matrices ranging from silicate rich to borate rich. The large variations in the characteristics of SiO_2 and B_2O_3 glasses (thermal expansion coefficients, softening temperatures, chemical durability, etc.) provide two contrasting systems for study. Large variations in microstructure (crystallite size and connection of phases) have been achieved depending on the composition and heat treatment conditions. The size of the $PbTiO_3$ crystallites can be varied from submicron to >10 µm. The effects of composition and processing on the resulting microstructure and electrical properties is being studied.

Glass powders of compositions in this system densify at 650°C, and crystallize the ferroelectric PT or PZT phases. The $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ composition, when pressed from a glass powder and heat treated to 850°C, produces piezoelectric d_{33} and g_{33} coefficients of 23 pC/N and 43×10^{-3} Vm/N, respectively. This appears to be the first research to crystallize PZT from glass (other than the PG based glass-ceramic research described in Section III). This research demonstrates the feasibility of developing piezoelectric glass-ceramics with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting.

VI. FERROELECTRIC THICK-FILMS

Microelectronic technology is continually expanding through the integration of different types of electronic components into multilayer ceramic packages. Resistor and capacitor components are currently incorporated in thin and thick-film circuits, while the integration of other types of components are under investigation. The focus of this research is to establish the potential of developing low-firing ferroelectric thick-films with useful piezoelectric properties. Commercial ferroelectric thick-films have been developed with high dielectric constants for capacitor applications. However, these compositions typically do not densify well at thick-film firing temperatures (850°C), and thus require encapsulants to provide environmental stability.

In this research crystalline lead zirconate-titanate (PZT) powder is being combined with amorphous $Pb_5Ge_2SiO_{11}$ (PGS) powder by J. Collier to produce a low firing piezoelectric composite material in bulk and thick-film form. The amorphous powder acts as a sintering aid, and then crystallizes into an additional ferroelectric phase which contributes to the electrical properties. The addition of PGS lowers the densification temperature, while also lowering the piezoelectric activity. At the typical thick-film firing temperature of 850°C, the 50/50 weight percent PZT/PGS composition densifies with a dielectric constant of 180 (at 1kHz) and a piezoelectric d_{33} coefficient of 20 pC/N at 25°C. These compositions could potentially be incorporated into low-fired multilayer packages as a sensor or actuator. Presentations on this research were given at the 1993 Annual Meeting of the American Ceramic Society, and at the 8th International Meeting on Ferroelectricity. Appendix 4 provides additional details on this research.

VII. PLANS FOR NEXT YEARS RESEARCH

- Establish the potential of developing a low-temperature processing method to produce useful piezoelectric and pyroelectric properties by crystallizing ferroelectric phases from amorphous compositions in the $Pb(Zr_{1-x}Ti_x)O_3$ - $Pb_5Ge_3O_{11}$ system.
- Compare the densification and crystallization behavior between solution-derived and melt-derived amorphous materials from these systems.
- Continue to investigate why PT and PZT additions have such a great effect on the orientation of PG in solution-derived thin films, but not in melt-derived thick films. Utilize the thin-film orientation to produce useful pyroelectric properties.

- Investigate the effect of thermal expansion mismatch between PG based compositions and the thin and thick-film substrates used. The high thermal expansion of PG appears to have resulted in cracking of films on alumina substrates, and thus higher expansion substrates, such as MgO, will be investigated.

- Complete the characterization of the densification and crystallization behavior and resulting piezoelectric properties of glass-ceramics in the PZT lead borosilicate system. The most promising compositions will be further optimized by investigating the effects of Zr/Ti ratio and other additives on properties.

- Evaluate the effects of interactions of electrodes and substrates in thin-film, thick-film, and tape-cast multilayer systems on the crystallization behavior and properties of the melt and solution-derived compositions developed.

- Establish the potential of achieving high dielectric constant compositions with low processing temperatures for thick-film capacitor applications by combining amorphous PGS powder with crystalline $0.93Pb(Mg_{1/3}Nb_{2/3})$-$0.07PbTiO_3$.

VIII. RESEARCH LABORATORIES

The funding for equipment provided in the first year of the ONR Young Investigator Award was combined with equipment support from the Colorado School of Mines, National Science Foundation, and Coors Ceramic Company to provide research laboratories for the processing and characterization of ceramic materials. The following is list of these facilities divided into two categories: property characterization and ceramic processing.

PROPERTY CHARACTERIZATION

- Dielectric Constant, Dissipation Factor, and Impedance (-184 to 315°C)
  - Computer Automated System
  - LCR Meter, HP4284A (20Hz to 1MHz)
  - RF Impedance Analyzer, HP4191A (1 MHz to 1GHz)
  - Temperature Chamber, Delta Design 9023-4-3-1

- Ferroelectric Hysteresis (to 4,000 V)
  - Ferroelectric Hysteresis Test System with High Voltage Interface, Radiant Technologies RT66A

- Piezoelectric Coefficients
  - Piezoelectric Charge Coefficient d_{33} Test System, Channel Products
  - Hydrostatic Piezoelectric Voltage Coefficient g_h Test System

- Pyroelectric Coefficient (-184 to 315°C)
  - Computer Automated System
  - pA Meter/DC Voltage Source, HP4140B
  - Temperature Chamber, Delta Design 9023-4-3-1

- Thermal Expansion and Differential Thermal Analysis (R.T. to 1600°C)
  - Computer Automated System
  - Dilatometer, Theta Dilamatic II RDP
  - DTA, Theta Labtronic II SDP

CERAMIC PROCESSING

- Sol-Gel Processing and Thin Film Spin Coating
  - Glove Box with Electronic Balance
  - Reaction Flasks/Condensers
  - Spin Coater (Integrated Technologies P6204) in a Class 100 Laminar Flow Hood

- Thick Film Screen Printing and Tape Casting
  - Screen Printer (Dek Model 250) in a Class 100 Laminar Flow Hood
  - Tape Caster

- Powder Processing and Pressing
  - HEPA Filtered Glove Box with Electronic Balance
  - Ball Mills
  - 12 Ton Lab Press, Carver Model C

- Glass Melting
  - 1725°C Glass Melting Furnace, Deltech DT-31-RS-OS-HWB
  - Pt and Pt/Rh crucibles
  - Rapid Roller Quenching Apparatus

- Firing
  - 1100°C Programmable Box Furnaces (2), Lindberg 51848
  - 1200°C Programmable Rapid Thermal Annealing Furnace
  - 1540°C Programmable Box Furnace, Applied Test Systems Series 3450
  - 1700°C Programmable Box Furnace, Lindberg 51524

- Electrical Poling (R.T. to 300°C; to 10,000 V)
  - High Voltage DC Power Supply, Trek 610C
  - High Temperature Oil Bath, Neslab EX-250HT

VII. PUBLICATIONS, MANUSCRIPTS, AND PRESENTATIONS

PUBLICATIONS (accepted for publication)

1. I. A. Cornejo, J. Collier, and M. J. Haun, "Ferroelectric and Crystallization Behavior in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ Glass-Ceramic System," Proceedings of the 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993; accepted for publication in *Ferroelectrics* (see Appendix 1).

2. S. M. Landin and M. J. Haun, "Solution-Derived Ferroelectrics in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," Proceedings of the 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993; accepted for publication in *Ferroelectrics* (see Appendix 2).

3. B. Houng and M. J. Haun, "Lead Titanate and Lead Zirconate Titanate Piezoelectric Glass-Ceramics," Proceedings of the 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993; accepted for publication in *Ferroelectrics* (see Appendix 3).

4. J. Collier, I. A. Cornejo, and M. J. Haun, "Ferroelectric Thick Films for Piezoelectric Applications," Proceedings of the 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993; accepted for publication in *Ferroelectrics* (see Appendix 4).

MANUSCRIPTS (submitted for publication)

1. M. J. Haun, I. A. Cornejo, J. Collier, S. M. Landin, Y. Kim, and B. Houng, "Processing Techniques for Crystal Alignment in Lead Germanate Based Compositions," Proceedings of the Sixth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Maui, HI, Nov. 11-12, 1993 (see Appendix 5).

MANUSCRIPTS (to be submitted for publication)

1. I. A. Cornejo and M. J. Haun, "Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part I - $Pb_5Ge_3O_{11}$-$PbTiO_3$ System," (see Appendix 7).

2. I. A. Cornejo and M. J. Haun, "Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part II - $Pb_5Ge_3O_{11}$-$PbTiO_3$ System," (see Appendix 8).

3. I. A. Cornejo, J. Collier, and M. J. Haun, "Water Induced Crystallization of a Metastable Phase from Melt Derived $Pb_5Ge_3O_{11}$ Based Amorphous Compositions," (see Appendix 9).

PRESENTATIONS

1. I. A. Cornejo and M. J. Haun, "Ferroelectric Glass-Ceramics Based on the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," 94th Annual Meeting of the American Ceramic Society, Minneapolis, MN, April 14, 1992.
2. M. J. Haun, "Glass-Ceramics for Electronic Applications," ONR Transducer Materials Review, The Pennsylvania State University, State College, PA, April 22, 1992.
3. M. J. Haun, I. A. Cornejo, J. Collier, B. Houng, and S. M. Landin, "Crystallization and Microstructural Control of Ferroelectric Glass-Ceramics and Thin-Films," ONR Transducer Materials Review, The Pennsylvania State University, State College, PA, April 7, 1993.
4. I. A. Cornejo and M. J. Haun, "Crystallization Behavior of $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ Ferroelectric Glass-Ceramics," 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, paper E-61-93, April 18-22, 1993.
5. J. Collier and M. J. Haun, "Ferroelectric Thick Films for Piezoelectric Applications," 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, paper E-83-93, April 18-22, 1993.
6. B. Houng and M. J. Haun, "Crystallization Behavior of Glass-Ceramics in the $PbTiO_3$-SiO_2 and $PbTiO_3$-B_2O_3 Systems," 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, paper EP-12-93, April 18-22, 1993.
7. S. M. Landin and M. J. Haun, "Solution-Derived Ferroelectrics in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, paper EP-37-93, April 18-22, 1993.
8. M. J. Haun, I. A. Cornejo, J. Collier, B. Houng, and S. M. Landin, "Crystallization and Microstructural Control of Ferroelectric Glass-Ceramics and Thin-Films," Mountain States Society of Electron Microscopists 1993 Spring Symposium, Lakewood, CO, May 13-14, 1993.

9. I. A. Cornejo, J. Collier, and M. J. Haun, "Ferroelectric and Crystallization Behavior in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ Glass-Ceramic System," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

10. S. M. Landin and M. J. Haun, "Solution-Derived Ferroelectrics in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

11. B. Houng and M. J. Haun, "Lead Titanate and Lead Zirconate Titanate Piezoelectric Glass-Ceramics," 8th International Meeting on Ferroelectricity, Gaithersburg,MD, Aug.8-13,1993.

12. J. Collier, I. A. Cornejo, and M. J. Haun, "Ferroelectric Thick Films for Piezoelectric Applications," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

ABSTRACTS ACCEPTED FOR PRESENTATION

1. M. J. Haun, S. M. Landin, I. A. Cornejo, J. Collier, B. Houng, and Y. Kim, "Crystallization Behavior of Ferroelectric Thin-Films and Glass-Ceramics," PAC RIM Meeting, Honolulu, HI, November 7-10, 1993.

2. M. J. Haun, I. A. Cornejo, J. Collier, S. M. Landin, Y. Kim, and B. Houng, "Processing Techniques for Crystal Alignment in Lead Germanate Based Compositions," Sixth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Maui, HI, Nov. 11-12, 1993.

VIII. GRADUATE STUDENT PARTICIPANTS

Graduate Students	Status	Source of Research Assistantship
Ivan A. Cornejo	Ph.D. Student in Materials Science	NSF PYI Award
Boen Houng	Ph.D. Student in Materials Science	ONR Young Investigator Award
Steven M. Landin	Ph.D. Student in Materials Science	AASERT Funding
James Collier	M.S. Student in Materials Science	ONR Young Investigator Award
Yangdo Kim	M.S. Student in Materials Science	NSF PYI Award

APPENDIX 1

PRESENTED AT THE 8th INTERNATIONAL MEETING ON FERROELECTRICITY, GAITHERSBURG, MD, AUGUST 8-13, 1993. TO BE PUBLISHED IN FERROELECTRICS.

FERROELECTRIC AND CRYSTALLIZATION BEHAVIOR IN THE $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ GLASS-CERAMIC SYSTEM

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Abstract The ferroelectric and crystallization behavior of glass-ceramic compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ system were investigated. Selected compositions were melted, quenched and milled into amorphous powders. Pressed samples crystallize completely into multiple ferroelectric phases at 600°C, and densify to 95-98% of the theoretical density at 700-720°C. Oriented thick-films were prepared by screen printing, followed by melting and recrystallization. By varying the heat treatment conditions the size of the PG, PT, and PZT crystallites were controlled from submicron to $>10\mu m$.

INTRODUCTION

Ferroelectric glass-ceramics have been used in capacitor, electro-optic, and hybrid circuit applications for many years,[1] but useful piezoelectric and pyroelectric properties were achieved only recently.[2] The critical crystallite size, microstructure, connectivity, amount and distribution of the ferroelectric phases (as well as the glassy phase) are critical parameters to achieve ferroelectricity in these materials, and especially to produce useful piezoelectric and pyroelectric properties. These parameters are still not well understood, and thus further research is needed.

$Pb_5Ge_3O_{11}$ (PG) is an unusual ferroelectric crystal, because it can be easily formed into a glass, due to the presence of the glass former GeO_2. The piezoelectric coefficients of PG are relatively low; however the pyroelectric properties are of interest for thermal detector applications. Ferroelectricity in $Pb_5Ge_3O_{11}$ was independently discovered by Iwasaki et al.,[3] and by Nanamatsu et al.[4] in 1971 in single crystals prepared by the Czochralski and Bridgman methods, respectively. The existence of $Pb_5Ge_3O_{11}$ single crystals confirmed the PbO-GeO_2 phase diagram work reported by Sperankaya[5] in 1959. In general, the lead germanate literature can be divided into three areas of research:[6-7] cation substitutions; sintering aid; and orientation. First, solid solution cation substitutions to $Pb_5Ge_3O_{11}$ have been made to increase the room temperature dielectric constant by reducing the ferroelectric to paraelectric phase transition temperature (Curie point of PG is 177°C) and to improve optical properties.[8-13] Second, the use of $Pb_5Ge_3O_{11}$, with a low melting point of

738°C, has been used as a sintering aid.[14-19] In this type of research up to thirty weight percent of crystalline PG has been mixed with other crystalline ferroelectric compounds, such as PZT or PLZT, to lower the processing temperatures, and to increase the density of the final product. Finally, lead germanate has also been used in thin and thick film forms to produce textured or oriented microstructures.[20-23]

In this paper, the crystallization behavior and resulting properties of amorphous compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ system is presented. The excellent piezoelectric properties of compositions in the $Pb(Zr_xTi_{1-x})O_3$ (PZT) solid solution system are well established, and have been extensively used for many years in a wide range of transducer applications. Thus, the PG-PZT system potentially combines the glass forming ability of PG with the excellent properties of PT or PZT, and provides a unique ferroelectric glass-ceramic system for study, where ideally 100% of the compositions can crystallize into ferroelectric phases.

EXPERIMENTAL PROCEDURE

Seven different compositions from the $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) and $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ (PG-PZT) systems were prepared from reagent grade Pb_3O_4, TiO_2, and ZrO_2, and electronic grade GeO_2. The batches were mixed for five hours and transferred to a platinum crucible for melting. The crucible was covered with a Pt-lid and placed into the furnace at temperatures from 800 to 1275°C, depending on composition with a hold time of fifteen minutes. The molten liquid was poured either into distilled water at 2°C or into a twin-roller quenching apparatus to produce glass ribbon. The glass obtained by these quenching methods was then ball milled in either distilled water or dry for twenty hours. After ball milling the slurry was screened through a 325 mesh (45 μm) sieve, and dried at 100°C. The dry milled powders were screened through a 200 mesh (75 μm) sieve. Pellets 13 mm in diameter and 1-2 mm thick were pressed without binder at a pressure of 10 ksi for one minute. After heat treatments at several temperatures and times, the samples were analyzed with XRD and SEM. Samples were also polished and electroded with sputtered gold followed by a layer of air-dried silver for electrical property measurements.

The amorphous powders were also prepared into thick film form. Initially, either a Ag/Pd DuPont 6134 paste or a platinum DuPont 9894 paste was screen printed on 96% Al_2O_3 substrates (Coors Ceramics Co.) to act as a bottom electrode. The glass powders were prepared into a thick film paste using an organic vehicle consisting of ethyl cellulose and pine oil, and screen printed onto the electroded alumina substrates. After drying at 150°C for 10 minutes, the organics were burned out at 350°C for 30 minutes and fired at 800°C for 30 minutes. A top gold electrode was applied by sputtering, followed by painting a layer of air-dried silver. XRD, SEM and electrical measurements were performed on the thick film samples.

RESULTS AND DISCUSSION

XRD patterns of the roller quenched powders are shown in Figure 1. The $Pb_5Ge_3O_{11}$, $3Pb_5Ge_3O_{11} \cdot PbTiO_3$, and $3Pb_5Ge_3O_{11} \cdot Pb(Zr_{1/2}Ti_{1/2})O_3$ compositions are x-ray amorphous. The other four compositions with further additions of PT or PZT are mostly amorphous, but have small crystalline peaks corresponding to the desired ferroelectric phases PG, PT, and/or PZT. However, the $Pb_5Ge_3O_{11} \cdot 3Pb(Zr_{1/2}Ti_{1/2})O_3$ composition also shows the ferroelastic and possibly antiferroelectric[24] Pb_3GeO_5 compound.

Figure 2 shows Differential Thermal Analysis (DTA) profiles on glass powders of the system PG-PT upon heating. Endothermic shifts occur in the baseline corresponding to the softening and densification of the glass powders. These shifts are composition dependent and occur at temperatures from 333 to 407°C (from 333 to 373°C for PG-PZT system, not shown). The degree of densification is controlled by the amount of crystalline material present, and the separation between the softening and crystallization processes. Exothermic crystallization peaks occur at temperatures from 385 to 473°C. The DTA curves (Figure 2) show a clear separation of the softening and crystallization temperature ranges indicating the potential of densification at very low temperatures ($<$ 407°C).

In the pure PG composition, the first crystallization peak at 385°C corresponds to the crystallization of a metastable nonferroelectric PG phase.[25] A small second exothermic peak occurs at 495°C where the metastable phase transforms to the stable ferroelectric PG phase.

Figure 2 also shows that the melting temperatures (endothermic peaks at around 740°C) decrease with the addition of PT. These results suggest that a eutectic point at around 730 °C occurs in the PG-PT phase diagram. A similar trend was observed in the PG-PZT system, with the exception of a dual melting point at $\approx$703°C in coexistence with that at 730°C. The PG•3PZT exhibits only the low melting point peak. This temperature corresponds to the eutectic point between $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 in the $PbO\text{-}GeO_2$[26] phase diagram.

On cooling (not shown) the PG-PT system, the DTA exhibits a large exothermic peak from recrystallization ranging from 715 to 703°C. In addition, a small exothermic peak occurs at lower temperatures around 475°C. This is believed to be a result of the latent heat of the discontinuous first order paraelectric to ferroelectric phase transition of $PbTiO_3$. $Pb_5Ge_3O_{11}$ and $Pb(Zr_{1/2}Ti_{1/2})O_3$ transform from a paraelectric to ferroelectric phase at 177°C and 390°C respectively; however these transitions are second order,[27-28] and thus a latent heat would not occur.

The results presented thus far have been on the quenched roller glass compositions prepared by dry ball milling. An interesting result occurred from ball milling these compositions in distilled water, where the glass crystallizes a phase that

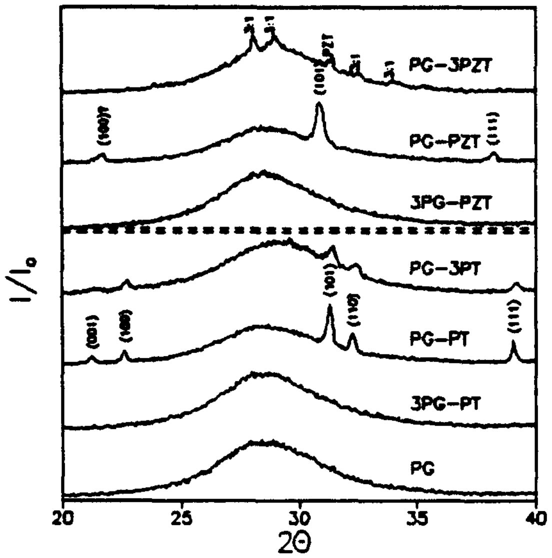

Figure 1 X-ray diffraction patterns of the PG-PT and PG-PZT roller quenched glasses.

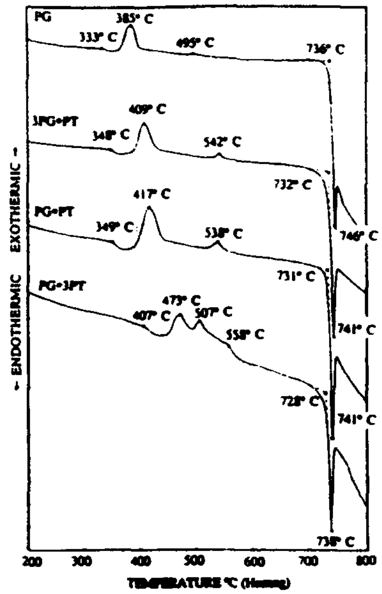

Figure 2 DTA patterns of the roller quenched PG-PT glasses heated at 10°C/min.

does not appear to match any of the JCPDS x-ray diffraction cards. A similar pattern was also found to occur after ball milling the other compositions (with PT and PZT additions) in water. Additional studies show that this unidentified metastable phase crystallizes from contact with water at room temperature without ball milling.

Pressed pellets of the glass powders that were ball milled in water densify to 95-98% of theoretical density at 700-720°C, and crystallize completely into the desired phases at ≤600°C. Figure 3 shows the x-ray diffraction patterns of the PG, PG • PT, and PG • PZT compositions after heat treatment at 720 °C for 20 hours. All peaks in the PG pattern correspond to the ferroelectric $Pb_5Ge_3O_{11}$ phase. Comparison of this pattern with the other two reveals additional peaks from the tetragonal $PbTiO_3$ phase in PG • PT, and from the perovskite (rhombohedral and/or tetragonal) PZT phase in PG • PZT. In addition, a few small PG(3:1) peaks occur in the PG • PZT composition.

The dielectric constants and dissipation factors were measured as a function of temperature at different frequencies (not shown). The dielectric constants form a peak because of the ferroelectric to paraelectric phase transition of the $Pb_5Ge_3O_{11}$ phase. The dielectric constant was found to increase at low temperatures as the PT and PZT content was increased, because of the higher dielectric constant contribution from the ferroelectric PT and PZT phases. The dissipation factor measurements also showed a peak at the PG transition. With PT addition the D.F. increases significantly at higher temperatures (from 0.5% at RT to 5% at 250°C at 1MHz) because of increased conduction losses, which is not seen with the addition of PZT.

Hysteresis loops and electrical poling of the bulk samples were not achieved with electric fields up to 30 KV/cm. However, on thick-films hysteresis loops were obtained. Figure 4 shows the ferroelectric hysteresis loop of a PG • PZT glass-ceramic

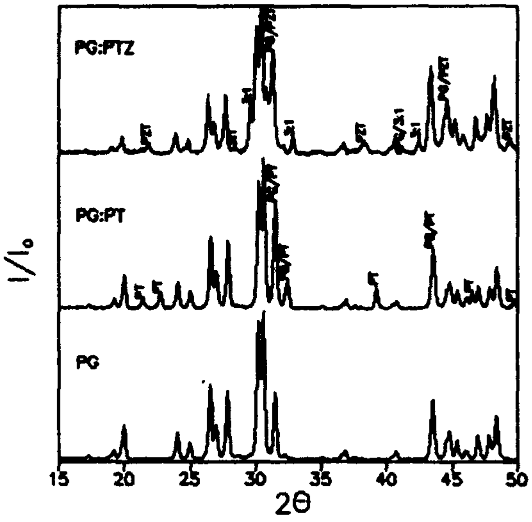

Figure 3 XRD patterns of selected compositions fired at 720°C, 20hr. Peaks not labeled = ferroelectric PG phase

film of 60 μm thickness screen printed on a 10μm Pt electrode on a 96 % Al_2O_3 substrate. The loop shows some non-saturation because of the high coercivity which resulted in electrical breakdown before saturation was complete. However, a maximum polarization of 7.2 $\mu C/cm^2$ was measured, which shows the influence of PZT on the polarization, since PG single crystals have a P_{max}[1,2] of 4-4.8 $\mu C/cm^2$.

Figure 5 shows an SEM micrograph of the surface of a PG•PZT thick film illustrating texture or orientation of the c-axis of the hexagonal $Pb_5Ge_3O_{11}$ crystal structure. Using a semi-quantitative relationship developed by F.G. Lotgering[29] a quality factor (F%) for the c-orientation is obtained from XRD data as listed in Table 1. The PG thick film on alumina without Pt electrode has an orientation of 60%, but on the Pt electrode this decreases to 17%. The additions of PT or PZT further decreases the c-orientation; however noticeable orientation still remains (Figure 5.)

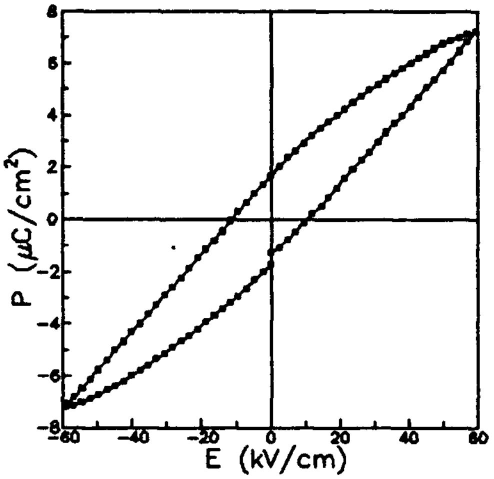

Figure 4 Hysteresis loop of a PG • PZT film melted at 850°C and cooled to 700°C for 1/2 hr.

Figure 5 SEM of PG • PZT screen printed on Pt electrode on Al_2O_3 substrate.

TABLE 1 Degree of c-orientation of PG-PT and PG-PZT systems of screen printed thick-films.

FILM	Orientation (F%)
PG/Al_2O_3	60
$PG/Pt/Al_2O_3$	17
$3PG \cdot PT/Pt/Al_2O_3$	5
$PG \cdot PT/Pt/Al_2O_3$	3
$3PG \cdot PZT/Pt/Al_2O_3$	12
$PG \cdot PZT/Pt/Al_2O_3$	4

SUMMARY

Compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ system were melted and prepared into glass powders. Some crystallization occurred depending on composition and quenching conditions. Reaction with water was found to crystallize an unidentified phase in all compositions, which transformed to the desired ferroelectric phases during heat treatment. The compositions crystallized multiple ferroelectric phases, and densified to 95-98% of theoretical density at 700-720°C. The sizes of PG, PT, and PZT crystallites can be controlled from submicron to $>10\mu m$ depending on the heat treatment conditions. Thick film samples were prepared with c-axis orientation of the hexagonal $Pb_5Ge_3O_{11}$ phase, and ferroelectric hysteresis loops measured.

ACKNOWLEDGEMENTS

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APPENDIX 2

Proceedings of the Eighth International Meeting on Ferroelectricity, Gaithersburg, Maryland
August 8-13, 1993 (To be Published in Ferroelectrics).

SOLUTION-DERIVED FERROELECTRICS IN THE $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ SYSTEM

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Abstract Ferroelectric thin films have promising potential in electronic applications, however the development and control of the required microstructure in order to obtain useful performance is currently a major technical challenge. This research investigates the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ (PG-PT-PZ) system. Compositions were formulated through a solution process leading to both bulk powders and thin films. Results on the phase development and microstructural orientation are presented relative to both composition and processing temperature.

INTRODUCTION

Ferroelectric thin films combine the unique electrical properties of ferroelectrics along with the useful geometric possibilities of thin film devices. Applications include nonvolatile memories, pyroelectric detectors, capacitors, SAW substrates and electro-optic devices. The properties required from the ferroelectric materials can vary greatly depending on the particular application.[1]

Lead germanate, $Pb_5Ge_3O_{11}$ (PG) has a ferroelectric-paraelectric phase transition at approximately 177°C. Single crystal PG is reported to have a dielectric constant of approximately 50 and a pyroelectric coefficient of 12×10^{-9} C/cm^2°C.[2] Even with this relatively low pyroelectric coefficient, the low dielectric constant makes PG an attractive candidate for pyroelectric elements. Polycrystalline PG has suppressed pyroelectric properties ($p = 5\times10^{-9}$ C/cm^2°C), however crystallographic orientation can increase the properties closer to those of the single crystal.[2] The [00l] is the direction of spontaneous polarization, and therefore has the maximum pyroelectric properties. Orientation of <00l> is readily achieved in PG due to the flat, hexagonal platelet geometry of the crystals. This orientation has been observed in both thin film[3] and thick film[4] PG compositions. The combination of PG with either PT or PZT offers a potentially unique combination of processing and electrical properties. These systems have been investigated to a limited extent.[5,6]

This paper investigates the phase development of solution derived powders in the PG-PT-PZ system. Phase development and c-axis orientation is reported for thin films prepared using a sol-gel technique for compositions of PG and PG-2PZT.

PROCEDURE

Compositions in the PG-PT-PZ system were prepared using a sol-gel technique. Precursors for the procedure included lead(II) acetate [$Pb(C_2H_3O_2)_2 \bullet 3H_2O$],[a] germanium ethoxide [$Ge(OC_2H_5)_4$],[b] titanium isopropoxide [$Ti(OC_3H_7)_4$][a] and zirconium n-propoxide [$Zr(OC_3H_7)_4$].[a] The processing followed successive stages of reflux/distillation in a solvent of 2-methoxyethanol [$C_3H_8O_2$].[a] Compositions were formulated as $Pb_5Ge_3O_{11}$ (PG), $Pb_5Ge_3O_{11}$-$2PbTiO_3$ (PG-2PT) and $Pb_5Ge_3O_{11}$-$2PbZr_{0.5}Ti_{0.5}O_3$ (PG-2PZT).

Using a final stock solution with a total cation concentration of 1M, bulk powders were produced by allowing the stock solution to gel for 96 hours at room temperature with final drying at 150°C. The dried gels were then crushed using a mortar and pestle before calcination.

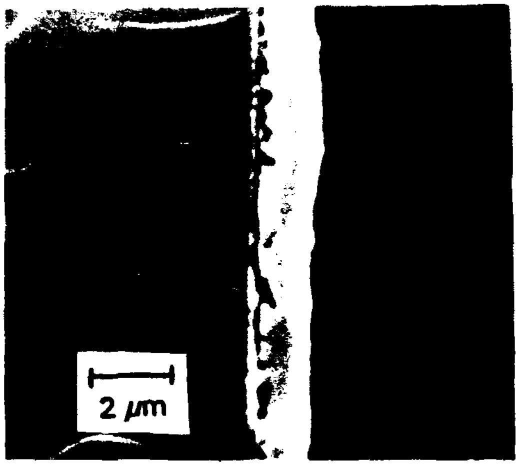

Figure 1. SEM micrograph of the fractured edge for PG on Pt/Si sintered at 700°C for 30 minutes (6,000X).

Thin films were produced by spin casting[c] the 1M stock solutions at 4000 RPM for 20 seconds. Residual organic removal was accomplished by annealing each layer at 300-400°C for 10 minutes before the next layer was applied. Four successive layers were spin cast and annealed followed by sintering for 30 minutes. An additional four layers were applied which were once again sintered for 30

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[a] Aldrich, Milwaukee, WI

[b] Gelest, Inc., Tullytown, PA

[c] Specialty Coating Systems, Inc., Indianapolis, IN, Model P6204

minutes. This procedure of building up eight layers resulted in final fired film thicknesses of between 1 and 1.5 microns (Fig.1). Three different substrate materials were investigated; borosilicate glass, platinum thick film fired on alumina, and platinized silicon.[d]

RESULTS AND DISCUSSION

Phase Development in Bulk Powders

X-ray diffraction performed on solution derived powders indicates that $Pb_5Ge_3O_{11}$ forms between 550 and 600°C in the compositions; PG, PG-2PT and PG-2PZT. Figure 2 shows that pyrochlore PT transforms to perovskite PT by approximately 600°C in the PG-2PT composition. Pyrochlore PZT showed similar behavior as the PT except that the pyrochlore phase did not transform to perovskite until 650°C. X-ray diffraction indicates that cation substitutions are very limited indicating that compositions within this system crystallize into multiple ferroelectric phases. Phase development in thin film samples closely followed that of the solution derived powders in terms of activation temperatures, however transformations at a particular temperature were much more rapid.

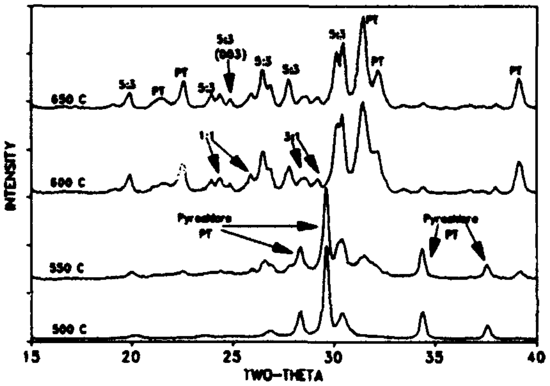

Figure 2. X-ray diffraction patterns for PG-PT solution derived powders with sintering times of 1 hour.

$Pb_5Ge_3O_{11}$ Thin Films

Lead germanate films exhibit a rapid orientation of the polar c-axis. A quality factor, F is used to describe the degree of orientation as described by Lotgerling.[7]

$$F=\frac{(P'-P_o)}{(1-P_o)} \qquad (1)$$

P_o is of non-oriented sample
P' is of oriented sample

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[d] Ramtron Corp., Colorado Springs, CO

$$P=\frac{Intensity\ of\ (00l)}{Intensity\ of\ All\ (hkl)} \tag{2}$$

Using this method, F=0 would correspond to a non-oriented structure, while F=1 would signify a perfectly oriented c-axis. The intensity of (003) was used in this study in the calculation of c-axis orientation. PG films on glass substrates show a rapid increase in (00l) orientation from 500 to 600°C (Fig.3). Films fired at 600°C for 30 minutes showed a c-axis orientation of nearly 60% (Table). Above 600°C, the films quickly lose their crystallographic order and become completely amorphous by 700°C. Lee and Dey[3] observed this behavior for PG thin films on Pt/Ti/SiO_2/Si substrates. They reported an unidentified phase at 600°C and a disappearence of 5-3 PG by 700°C. In the current study, this behavior between 600 and 700°C was only observed with glass substrates. PG films sintered on platinum/silicon substrates showed an increase in orientation with increased sintering temperature (Fig.4). For these samples, c-axis orientations of 38% were observed for films fired at 700°C for 30 minutes. PG films formed on platinum thick film/alumina substrates followed a similar behavior to that of the films on Pt/Si, however the degree of orientation was reduced (Table).

The dielectric constant of the PG films on platinum thick film and Pt/Si with orientations up to 38% show peaks at approximately 177°C, indicating the ferroelectric-paraelectric phase transition. These values were in the range of 80 at 100KHz. Room temperature dielectric constants ranged between 30 and 40. These values are similar to those found in randomly oriented polycrystalline samples.

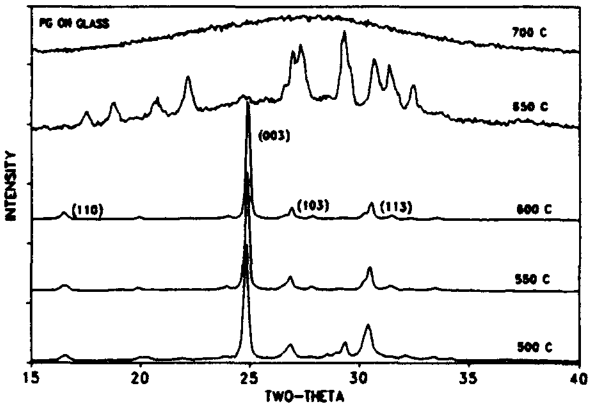

Figure 3. X-ray difraction patterns for $Pb_5Ge_3O_{11}$ thin films on glass substrates for 30 minute firing times.

$Pb_5Ge_3O_{11}$-$PbZr_{0.5}Ti_{0.5}O_3$ Thin Films

Films with a composition of PG-2PZT, corresponding to 70 weight % PG and 30 weight % PZT, fired on platinum/silicon substrates showed (00l) orientations greater than 90% for firing temperatures of between 600 and 750°C (Fig.5)(Table). This orientation is greater than any obtained with the PG composition.

TABLE. C-axis orientation of thin films.

Thin Film Type	Temperature(°C)	F(%)
PG on Glass	500	41
	550	57
	600	59
PG on Pt Thick Film/Alumina	550	14
	600	17
	650	21
	700	20
PG on Pt/Si	550	11
	600	25
	650	33
	700	38
PG-PZT on Pt/Si	650	>90
	700	>90
	750	>90

The PG(003) line appears to be shifting to a slightly lower d-spacing (higher 2-θ) with increasing temperature, however this may actually be a transformation from an oriented metastable hexagonal 5-3 phase, represented by its (008) diffraction line, to the stable hexagonal 5-3 phase. The metastable (008) line is reported by Otto[8] to be located at d = 3.63 while the (003) line of the stable phase is reported at d = 3.56.[9] Experimental d-spacings for this line were determined to be 3.64 at 600°C and 3.57 at 750°C. The PG(006) line appears to show a similar shifting/transformation to a lower d-spacing.

The lead germanate peak in the dielectric constant for this composition was shifted to a slightly higher temperature, 180°C, with values in the range of 80 at 100kHz.

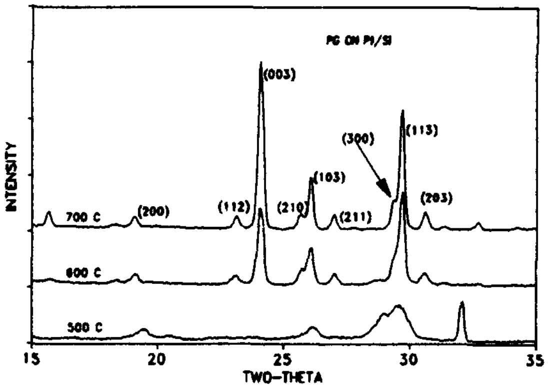

Figure 4. X-ray diffraction patterns for $Pb_5Ge_3O_{11}$ thin films on Pt/Si substrates for 30 minute firing times.

SUMMARY

Solution derived powders with compositions PG, PG-2PT and PG-2PZT were observed to form the 5-3 ferroelectric phase of PG between 550 and 600°C. In the PG-PT system, pyrochlore PT transformed to perovskite by approximately 600°C while the pyrochlore PZT to perovskite transformation was observed at 650°C. PG thin films show rapid orientation of the c-axis which increased with increasing temperature. PG thin films on glass substrates were observed to lose their crystallographic structure above 650°C. Thin films in the PG-2PZT system show c-axis orientations of the PG 5-3 phase in excess of 90% for sintering temperatures between 650 and 750°C.

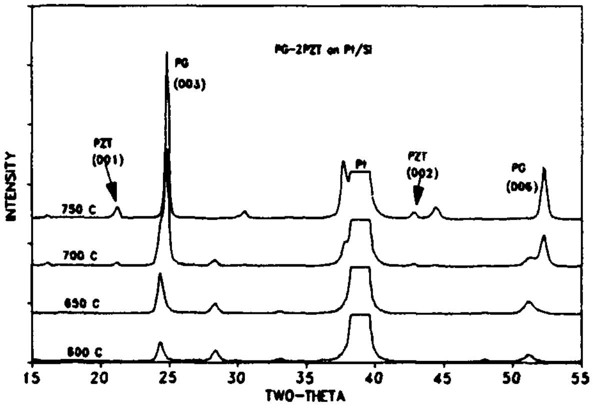

Figure 5. X-ray diffraction patterns for $Pb_5Ge_3O_{11}$-$2PbZr_{0.5}Ti_{0.5}O_3$ thin films on Pt/Si substrates for 30 minute firing times.

ACKNOWLEDGEMENT

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APPENDIX 3

Proceedings of the 8th International Meeting on Ferroelectricity, Aug 9-13, 1993, to be published in Ferroelectrics

LEAD TITANATE AND LEAD ZIRCONATE TITANATE PIEZOELECTRIC GLASS-CERAMICS

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Abstract The crystallization behavior and electrical properties of a piezoelectric glass-ceramic system consisting of lead titanate (PT) or lead zirconate titanate (PZT) in a lead borosilicate matrix is presented. Glass powders of compositions in this system densify at 650°C, and crystallize the ferroelectric PT or PZT phases. $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ is provided as an example of a composition that when pressed from a glass powder and heat treated to 850°C produces piezoelectric d_{33} and g_{33} coefficients of 23 pC/N and 43×10^{-3} Vm/N, respectively. Results are also presented for a previously developed PT based glass-ceramic for comparsion.

INTRODUCTION

Glass-ceramics are utilized in a wide variety of applications, and many useful techniques are established to control the crystallization behavior, microstructural development, and resulting properties.[1] The development of ferroelectric glass-ceramic compositions with useful piezoelectric properties will allow the advantages of glass-ceramic processing, such as forming methods and lower heat treatment temperatures, to be utilized. Glass powders of these compositions can be prepared into pastes for screen printing onto thick-film circuits or into slurries for tape casting and integration into multilayer packages. The low firing temperatures inherent in glass-ceramic materials allow for potential compatibility with existing thick film conductors, dielectrics, and resistors. The purpose of this research was to establish the potential of developing ferroelectric glass-ceramics with useful piezoelectric properties that can be processed at low temperature (<900°C).

Ferroelectric glass-ceramics have been used in capacitor, electro-optic, and hybrid circuit applications for many years,[2] but useful piezoelectric properties were achieved only recently.[3,4] In this paper an evaluation of the processibility in powder and ribbon form of these previously developed $PbTiO_3$ (PT) based glass-ceramic compositions[3,4] is presented, and compared to that of newly developed $Pb(Zr_xTi_{1-x})0_3$ (PZT) based piezoelectric glass-ceramics.

EXPERIMENTAL PROCEDURE

A wide range of compositions were studied in the $xPb(Zr_yTi_{1-y})O_3 \cdot zPbO \cdot wSiO_2 \cdot uB_2O_3$ system, where x=0.6 or 0.8, y=0 or 0.52, z=0-0.28, w=0-0.4, and u=0-0.4. In addition, the $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ composition developed by Wu and Zhu[3,4] was also included in the investigation. The starting materials were reagent grade Pb_3O_4, TiO_2, ZrO_2, $SrCO_3$, MnO_2, Nb_2O_5, B_2O_3, and SiO_2. Pb_3O_4 was chosen as a starting material instead of PbO to reduce the possibility of reduction to metallic lead and subsequent reaction with the platinum crucible.

The batches were mixed by ball milling with zirconia media in methanol for 12 hours, dried at 50°C, and transferred to a platinum crucible for melting. The batches were placed into a furnace and melted for 15 minutes at 1100-1300°C depending on composition. The molten liquid was then quenched by pouring into a twin-roller quencher to form glass ribbon. Glass powder was prepared from the ribbon by ball milling in methanol with zirconia media for twenty-four hours. The glass powder was pressed into pellets without binder at a pressure of 10,000 psi. The pressed pellets (10 mm in diameter and 1-2 mm thick) and pieces of glass ribbon (100 µm x 5 mm x 5 mm) were heated on a platinum sheet up to various temperatures ranging from 650 to 1200°C at a rate of 10°C/min and held for 1 hour.

The resulting glass-ceramic samples were ground into powder for x-ray diffraction, and polished and electroded with sputtered gold followed by a layer of air-dried silver paint for electrical properties measurements. The dielectric constant was measured at 10 KHz on a Hewlett Packard HP4284A LCR meter. Ferroelectric hysteresis loops were measured with a Radiant Technologies RT66A Test System. The samples were then poled for 30 minutes at 180°C. The microstructures were also analyzed with SEM.

RESULTS AND DISCUSSION

Amorphous glass ribbon was easily formed by roller quenching compositions in the $xPb(Zr_yTi_{1-y})O_3 \cdot zPbO \cdot wSiO_2 \cdot uB_2O_3$ system with $w + u \geq 0.2$. However, with $w + u < 0.2$ partially crystallized ribbon was usually formed. The results presented in this section are focused on a selected composition,

$60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$, with comparison to the results of the $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ composition.

X-ray diffraction patterns of the $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ composition as-quenched and after heat treatment at various temperatures are shown in Figure 1. The as-quenched glass was x-ray amorphous. Heat treatment at 650°C crystallized two phases, perovskite PZT and Pb_2SiO_4. With crystallization of Pb_2SiO_4 a silica rich residual glass will develop in this composition potentially increasing the durability. In addition, this crystallization may lead to improve connectivity of the PZT phase for electrical poling. As the heat treatment temperature is increased the ratio of PZT to Pb_2SiO_4 also increases, indicating that PZT crystallized at a higher temperature than Pb_2SiO_4.

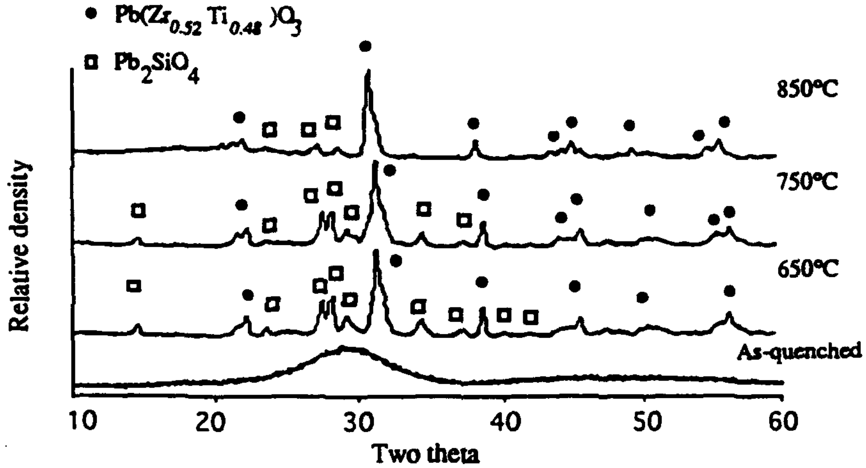

FIGURE 1 X-ray diffraction patterns of $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ as-quenched and heat treated at various temperatures.

Figures 2(a)-2(c) are SEM micrographs of the $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ composition in pressed form heat treated at 650, 750 and 850°C, respectively. At 650°C the composition densified, and with increasing heat treatment temperature the grain size increases to around 2-3 μm at 850°C.

X-ray diffraction patterns of the $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ composition are shown in Figure 3 after heat treatment at 750-950°C with a hold time of one hour. All of the crystalline peaks correspond to the perovskite $PbTiO_3$ phase with possible solid solubility of the Sr, Mn, and Nb. A· 950°C the $PbTiO_3$ becomes more tetragonal with the axial ratio (c/a) increasing to 1.046 [determined from the (112) and (211) peaks]. Pressed

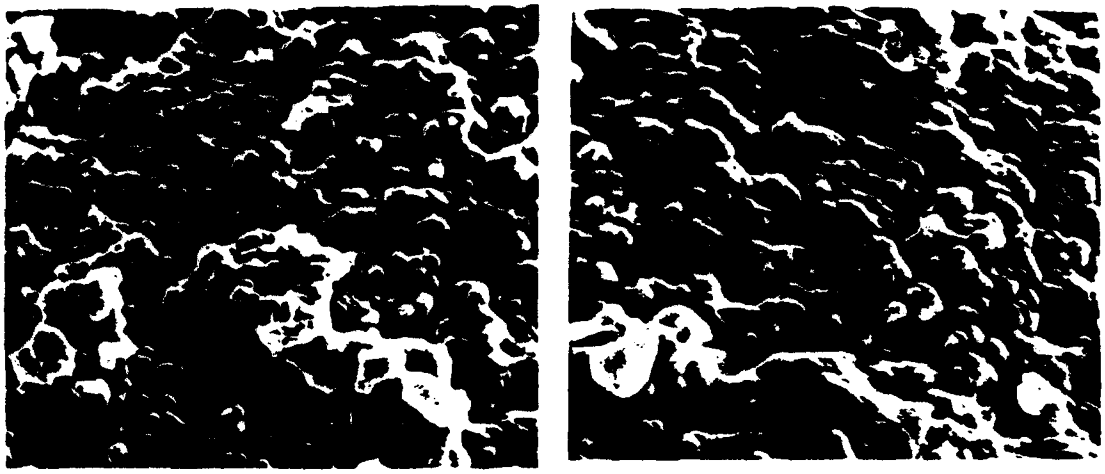

Fig. 2(a) Fig. 2(b)

Fig. 2(c)

FIGURE 2 SEM photographs of $60Pb(Zr_{0.52}Ti_{0.48})O_3$-$20PbO$·$20SiO_2$ heat treated at a) 650°C, b) 750°C and c) 850°C.

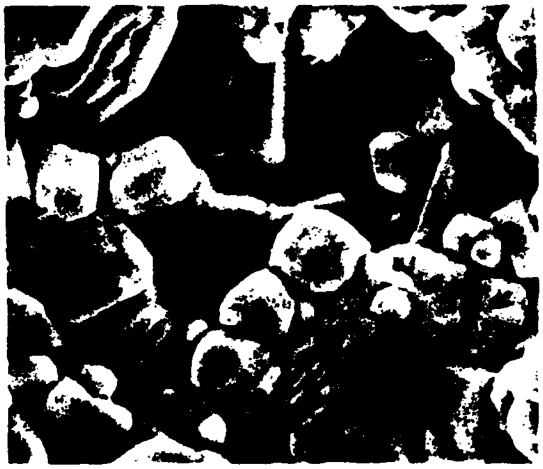

FIGURE 4 SEM photograph of $85(Pb_{0.85}$-$Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3$·$5Al_2O_3$·$10SiO_2$ heat treated at 1100°C.

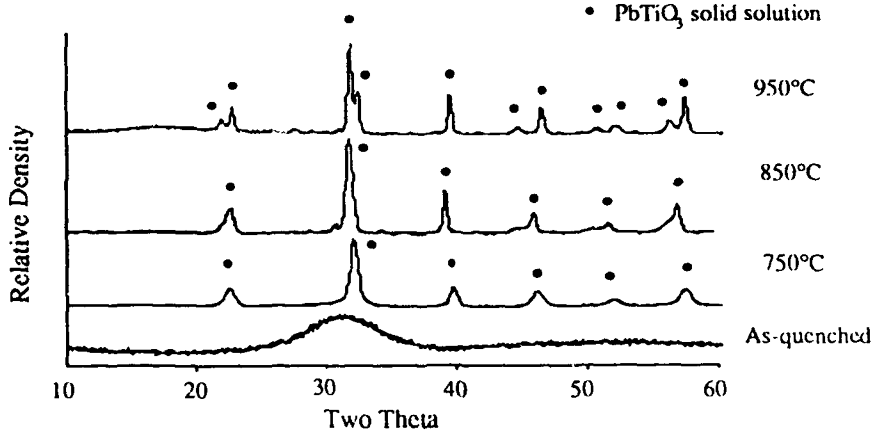

FIGURE 3 X-ray diffraction patterns for composition $85(Pb_{0.85}Sr_{0.15})$ $(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3$·$5Al_2O_3$·$10SiO_2$ heat treated at various temperatures.

pellets of glass powder of this composition did not densify to closed porosity until 1100°C. Figure 4 shows an SEM micrograph of the microstructure that develops from an 1100°C firing for one hour.

Ferroelectric hysteresis loops of heat treated glass of both compositions are shown in Figures 5(a) and (b). The spontaneous and remnant polarizations increased with increasing heat treatment temperature, with the PT glass-ceramic [Figure (5b)] having considerably higher values compared to the PZT glass-ceramic [Figure (5a)]. The coercive fields were also considerably higher for the PT glass-ceramic compared to the PZT glass-ceramic, corresponding to the larger tetragonality present.

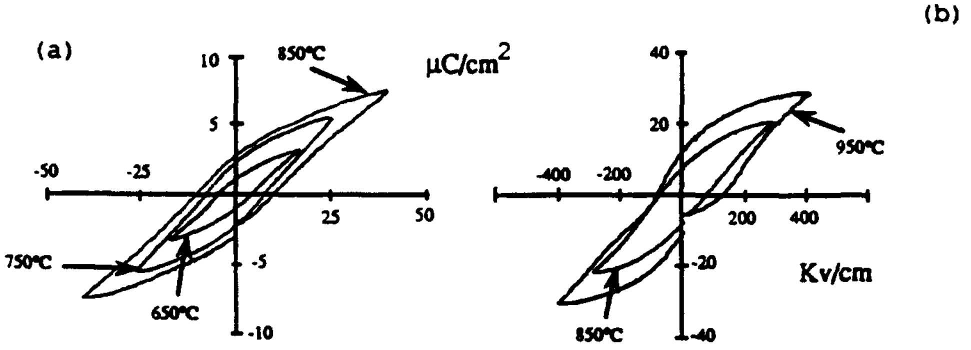

FIGURE 5 Ferroelectric hysteresis loops for (a) $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ and (b) $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ heat treated at various temperatures.

Table 1 provides a summary of the electrical properties of both compositions in pellet and ribbon form. The pressed glass powder (pellet) of the $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ composition did not densify adequately for electrical measurements below 1100°C, and thus only the 1100 and 1200°C data are listed. In comparison the $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ composition in powder form densified at 650°C. The glass ribbon samples were already dense, and thus only required heat treatment for crystallization. The PZT glass-ceramic has lower dielectric constant, dissipation factor, spontaneous and remanent polarization, and coercive field compared to the PT glass-ceramic, however similar piezoelectric d_{33} coefficients and higher g_{33} coefficients resulted with lower processing temperatures, especially in pressed powder form.

Table 1 Summary of the electrical properties of $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ and $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ compositions. (Ps is the maximum polarization value from the hysteresis loops.)

Electrical properties	$85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$					$60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$					
	Pellet		Ribbon			Pellet			Ribbon		
	1100°C	1200°C	750°C	850°C	950°C	650°C	750°C	850°C	650°C	750°C	850°C
K' (at 10KHz)	115	122	82	105	120	41	50	61	60	66	73
D.F. (%)	2.0	2.2	2.4	2.5	2.8	1.2	1.2	1.3	0.6	0.6	0.7
Ps ($\mu C/cm^2$)	10	12	14	18	26	0.3	0.8	2.7	2.4	5.7	7.5
Pr ($\mu C/cm^2$)	4.5	5.6	2.6	6.5	10.2	0.04	0.17	0.94	0.76	2.4	3.2
Ec (Kv/cm)	58	65	58	78	97	1	5	12	9	25	41
d_{33} (pC/N)	18	20	-	-	30	-	-	23	-	18	30
g_{33}(10^{-3} Vm/N)	17	19	-	-	28	-	-	43	-	30	46

SUMMARY

The crystallization behavior and electrical properties of a series of PT and PZT based glass-ceramics with lead borosilicate matrices have been investigated. Results for the $60Pb(Zr_{0.52}Ti_{0.48})O_3 \cdot 20PbO \cdot 20SiO_2$ composition were compared to a previously developed[3,4] $85(Pb_{0.85}Sr_{0.15})(Ti_{0.94}Mn_{0.02}Nb_{0.04})O_3 \cdot 5Al_2O_3 \cdot 10SiO_2$ composition. The PZT glass-ceramic composition in powder form densified at 650°C, while the PT glass-ceramic did not densify until 1100°C. Similar piezoelectric d_{33} coefficients resulted in the PZT glass-ceramic, and because of the lower dielectric constant higher g_{33} coefficients resulted. This research demonstrates the feasibility of developing piezoelectric glass-ceramics with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting.

ACKNOWLEDGEMENTS

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APPENDIX 4

PRESENTED AT THE 8th INTERNATIONAL MEETING ON FERROELECTRICITY, GAITHERSBURG, MD, AUGUST 8-13, 1993. TO BE PUBLISHED IN FERROELECTRICS.

FERROELECTRIC THICK-FILMS FOR PIEZOELECTRIC APPLICATIONS

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Abstract Crystalline lead zirconate-titanate (PZT) powder was combined with amorphous $Pb_5Ge_2SiO_{11}$ (PGS) powder to produce a low firing piezoelectric composite material. The amorphous powder acts as a sintering aid, and then crystallizes into an additional ferroelectric phase which contributes to the electrical properties. Piezoelectricity was observed both in thick-films and pellets fired at 850°C, suggesting that this material could potentially be incorporated into low fired multilayer packages as a sensor or actuator.

INTRODUCTION

Microelectronic technology is continually expanding through the integration of different types of electronic components into multilayer ceramic packages.[1] Resistor and capacitor components are currently incorporated in thin-film and thick-film circuits, while the integration of other types of components are under investigation. The focus of this research is to establish the potential of developing low-firing ferroelectric thick-films with useful piezoelectric properties. Commercial ferroelectric thick-films have been developed with high dielectric constants for capacitor applications. However, these compositions typically do not densify well at thick-film firing temperatures (≈850°C), and thus require encapsulants to provide environmental stability.

A variety of approaches have been investigated to lower the processing temperatures of ferroelectric materials for capacitor and piezoelectric applications, such as by additions of glass phases[2-7] or low melting crystalline phases.[8-19] One approach has involved additions of $Pb_5Ge_3O_{11}$[8-10,14] or $Pb_5(Ge_{1-x}Si_x)_3O_{11}$.[11-12] These lead germanate and lead germanium silicate compositions have low melting temperatures (≤738°C), and are unusual ferroelectrics which can be formed relatively easily into glasses, because of the presence of the glass formers GeO_2 and SiO_2.

Crystalline $Pb_5Ge_3O_{11}$ has been added to PLZT,[8] PZT,[9] and $Pb(Fe_{2/3}W_{1/3})O_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$[14] to form a low melting liquid phase and reduce the sintering temperature. Schulze and Biggers[9] also demonstrate an additional benefit of stabilizing the PZT phase from depoling by incorporating an insulating grain boundary phase. $Pb_5Ge_3O_{11}$ has also been investigated as a sintering aid for non-ferroelectric pyrochlore phases.[20]

Payne et al. extended their earlier work of combining $Pb_5Ge_3O_{11}$ with $BaTiO_3$[10] to also include additions of lead germanium silicate.[11-12] The starting PG and PGS compositions were prepared by melting, but the authors do not indicate whether the resulting powders were crystalline or amorphous.[10-12] $Pb_5Ge_{1.95}Si_{1.05}O_{11}$ has also been described as a suitable sintering aid for $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$-$Pb(Fe_{2/3}W_{1/3})O_3$.[16]

In this paper, the previous research is extended by combining PZT with amorphous $Pb_5Ge_2SiO_{11}$ (PGS) powders. Advantages of sintering PZT with amorphous PGS versus crystalline PGS are homogeneity, softening, and densification. PGS glass has a low softening point, 326°C, in addition to a low melting point, 724°C. Substituting silicon for germanium increases the glass formability and the room temperature dielectric constant, while lowering the melting temperature and Curie point.[21] In this system, PGS softens and densifies at low temperatures, and then crystallizes into a second ferroelectric phase. The experimental procedure used to prepare and characterize compositions in the PZT-PGS system is described in the next section, followed by a discussion of the crystallization behavior and the dielectric and piezoelectric properties.

EXPERIMENTAL PROCEDURE

In this section, the procedures used to prepare glass powders, thick-film and bulk samples, and to measure electrical properties are discussed. To prepare amorphous PGS, Pb_3O_4, GeO_2, and SiO_2 were first wet mixed by ball milling in a nalgene jar with water and zirconia media. After drying, the mixture was melted in a platinum crucible for 20 minutes at 810°C, and quenched into a twin roller quenching apparatus consisting of counter rotating steel cylinders. The resulting amorphous ribbon was then dry ball milled with zirconia grinding media for 24 hours, and sieved through 200 mesh (75 μm). SEM analysis revealed that the final powders had a particle size of approximately 1-10 μm.

A commercial 1 μm particle size modified PZT powder, Ultrasonic Powders 501A, was mixed with the amorphous PGS powder in compositions from 0-100 wt. % PGS. To press pellets, 3 wt. % pine oil was added to the powders as a binder and pressed at 10 ksi. Sintering temperatures of 620 and 850°C were used, depending on composition. Finally, electrodes were applied by sputtering a layer of gold followed by a layer of air dry silver paint. For screen printing, the PZT-PGS mixtures were combined with 30 wt.% vehicle consisting of a 1:9 weight ratio of ethyl cellulose and pine oil. Thick-film conductor pastes of silver/palladium (DuPont 6134) or platinum (DuPont 9894) were screen printed on 96% alumina substrates (Coors Electronics), dried at 150°C for 10 minutes, and fired at 850°C for 30 minutes for the Ag/Pd paste, and 1300°C for 60 minutes for the Pt paste. The PZT-PGS paste was printed over an area of 2.8 cm^2 on these conductors with a 200 mesh screen. Five PZT-PGS layers were separately printed, dried at 150°C for 10 minutes, and fired at 850°C for 30 minutes with a ramp rate of 10°C/min. A top electrode was deposited by sputtering gold.

The dielectric constant was measured at 1 kHz on a Hewlett Packard HP4284A LCR meter. Ferroelectric hysteresis loops were measured with a Radiant Technologies RT66A Test System. The samples were then poled for 30 minutes at 150°C with the same voltage as the maximum voltage applied during the ferroelectric hysteresis loop measurements. The chosen poling temperature was above the Curie point of PGS, but was necessary for adequate poling of the PZT phase. The piezoelectric d_{33} coefficient was measured on a Berlincourt d_{33} meter (Channel Products Company).

RESULTS AND DISCUSSION

In this section, the effects of composition and processing on the resulting phases and electrical properties are presented. Figure 1 shows x-ray diffraction patterns for the bulk samples with 0-50 wt. % PGS fired at 850°C. The only major crystalline phases detected are PZT and $Pb_5Ge_2SiO_{11}$ (which crystallized during firing).

Figure 2 displays the percent theoretical density as a function of PGS content with firing at 620 and 850°C. Softening of PGS glass aids in densification of this system as is evident from the high PGS content compositions fired at 620°C. The 100% PGS composition densified to more than 96% of the theoretical density, well below the melting point of PGS (724°C). At 620°C the density decreases almost linearly with additions of crystalline PZT. At 850°C, a 50 wt. % PGS sample produced a near closed porosity sample with a density about 88% of the calculated theoretical density of the ferroelectric composite. Again, with increasing additions of crystalline material, the density quickly decreases.

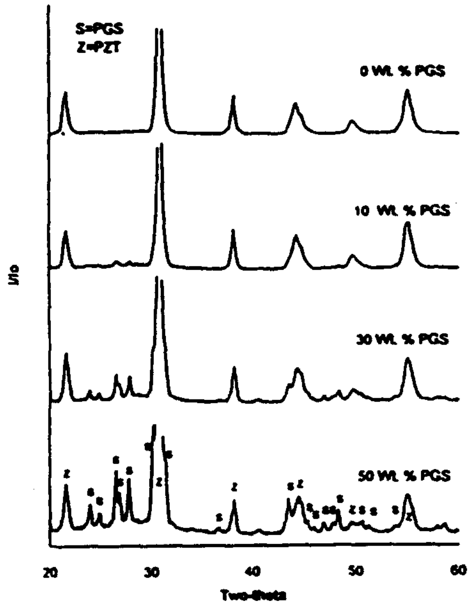

Figure 1 X-ray diffraction patterns of bulk samples sintered at 850°C showing additions of PGS into PZT.

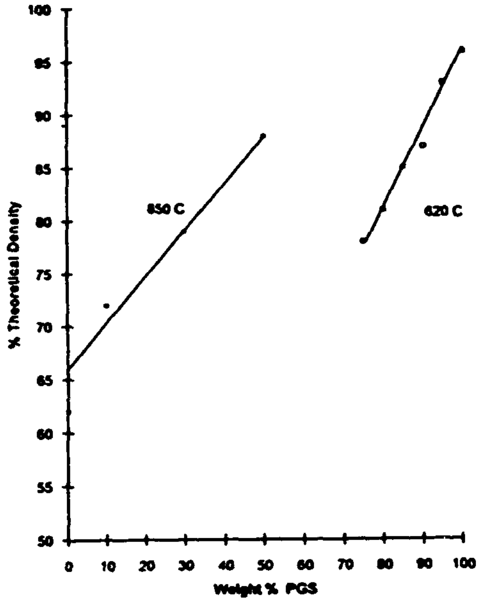

Figure 2 Percent theoretical density of bulk samples sintered at 850°C (■) and 620°C (□) as a function of PGS content.

The dielectric constant and dissipation factor of unpoled samples fired at 850°C are plotted versus the PGS content in Figure 3. The curves on the left are for the bulk samples, while those on the right are thick-film samples with platinum electrodes. The change in dielectric constant with PGS additions corresponds to the balance between densification and the ratio of the higher dielectric constant PZT phase to the lower dielectric constant PGS phase. Thick-films electroded with Ag/Pd saw an increase in dielectric loss with an increase in initial glass content (not shown), indicating that there is some interaction between this conductor paste and the PZT-PGS.

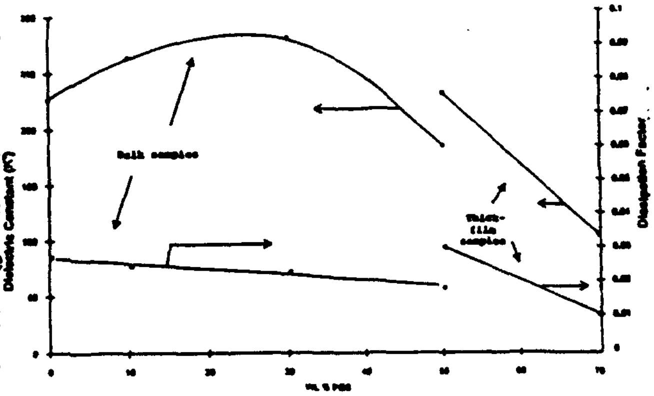

Figure 3 Dielectric constant and dissipation factor for bulk (left) and thick-film (right) samples fired at 850°C.

Figures 4 and 5 show the ferroelectric hysteresis loops in thick-film samples for compositions 0-70 wt.% PGS. Increasing the PGS content decreases the spontaneous polarization, remanent polarization, and coercive field for both platinum and Ag/Pd electrodes. The 50 wt.% PGS sample printed on platinum has a larger spontaneous polarization than the 10 and 30 wt. % PGS which are printed on Ag/Pd, indicating interaction between the Ag/Pd conductor paste and the PZT-PGS system.

The piezoelectric d_{33} coefficient of bulk samples fired at 850°C is plotted versus PGS content in Figure 6. With increasing PGS content the d_{33} coefficient decreases. The 50 wt.% PGS composition with the highest density has a d_{33} coefficient of 20 pC/N.

SUMMARY

Crystalline PZT and amorphous $Pb_5Ge_2SiO_{11}$ were combined and prepared into bulk and thick-film samples. The low softening and melting temperatures of the PGS glass allows low temperature densification of compositions in this system. During firing the PGS glass crystallized to the ferroelectric $Pb_5Ge_2SiO_{11}$ phase. The 50/50 weight% PZT/PGS composition densified to 88% of the calculated theoretical density at 850°C with a dielectric constant of 180 (at 1kHz) and a piezoelectric d_{33} coefficient of 20 pC/N at 25°C.

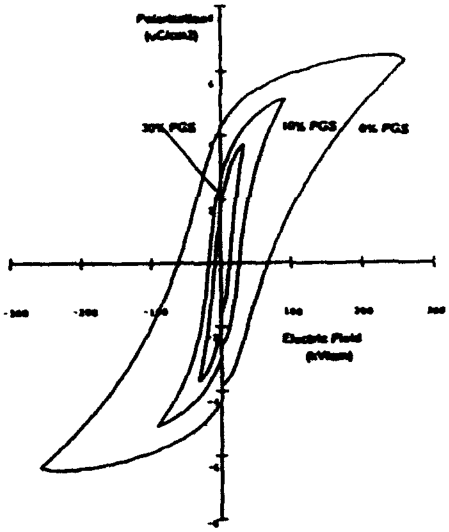

Figure 4 Ferroelectric hysteresis loops of PZT-PGS films fired at 850°C on Ag/Pd electrodes.

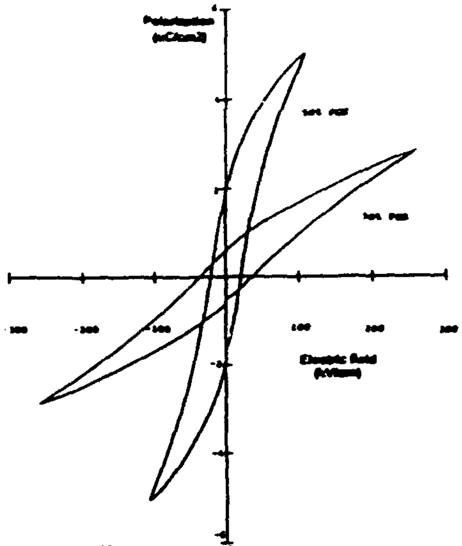

Figure 5 Ferroelectric hysteresis loops of PZT-PGS thick films fired at 850°C on Pt electrodes.

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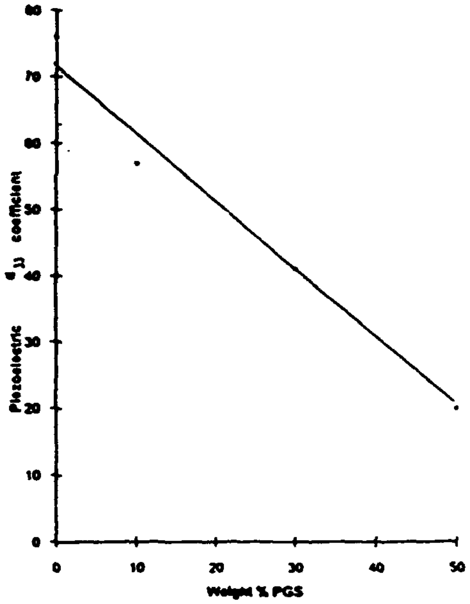

Figure 6 Piezoelectric d_{33} coefficient of pellets sintered at 850°C as a function of PGS content.

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APPENDIX 5

Proceedings of the Sixth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Maui, HI, Nov. 11-12, 1993.

PROCESSING TECHNIQUES FOR CRYSTAL ALIGNMENT IN LEAD GERMANATE BASED COMPOSITIONS

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ABSTRACT

Processing techniques were investigated to produce c-axis orientation of ferroelectric $Pb_5Ge_3O_{11}$ (PG) during crystallization of amorphous films of compositions from the $Pb_5Ge_3O_{11}$-$PbZr_xTi_{1-x}O_3$ system. These compositions crystallize into multiple ferroelectric phases with low processing temperatures. Solution-derived and melt-derived processing methods were used to prepare thin and thick-film, glass ribbon, tape cast, and bulk samples. Addition of $PbTiO_3$ or $PbZr_xTi_{1-x}O_3$ to PG results in decreased c-axis orientation of the PG crystallites in thick-film samples, however significantly enhanced orientation occurs in thin-film form.

INTRODUCTION

Ferroelectricity in $Pb_5Ge_3O_{11}$ (PG) was independently discovered by Nanamatsu et al.[1] and Iwasaki et al.[2] in 1971 in single crystals prepared by the Czochralski and Bridgman methods, respectively. The piezoelectric coefficients of PG are relatively low, however the combination of pyroelectric and dielectric properties are of interest for thermal detector applications. At the Curie point of PG (≈177°C) a slight distortion occurs from a high temperature paraelectric hexagonal structure to a low temperature ferroelectric trigonal structure. The spontaneous polarization develops along the c-axis of the trigonal state with only 180° domains possible.[3] Polycrystalline PG has suppressed pyroelectric properties compared to those of the single crystal. However, by crystallization of amorphous PG films orientation of the c-axis perpendicular to a substrate can be achieved, because of the flat platelet geometry of the crystals. This orientation has been accomplished by melting PG on gold foil, followed by controlled cooling to crystallize large c-axis oriented crystals.[3,4] Orientation has also been accomplished by heat treatment of amorphous ribbon,[5-7] and by utilizing thin[8-10] and thick-film processing.[11,12] These methods are potentially simpler and less expensive compared to single crystal techniques for producing thin large area infrared detectors.

Another interesting feature of PG is that it can be formed relatively easily into a glass,[13] because of the presence of the glass former GeO_2. In addition, the low melting point of PG (≈737°C) has allowed it to be used as a sintering aid in ferroelectric compositions for capacitor and piezoelectric applications.[14-19] PG has been combined with $PbTiO_3$ (PT) and $PbZr_xTi_{1-x}O_3$ (PZT) in amorphous form to provide unique ferroelectric glass-ceramic systems for study, where ideally 100% of the compositions can crystallize into multiple ferroelectric phases.[20-21] Compositions in the PG-PT and PG-PZT systems potentially combine the glass forming ability and low melting temperature of PG with the excellent properties of PT or PZT. The high PG compositions are being investigated for pyroelectric applications, while the high PT and PZT compositions are being studied for piezoelectrics with low processing temperatures. In this paper, the effects of processing method and composition (in the PG-PT and PG-PZT systems) on the orientation of the PG phase is discussed.

EXPERIMENTAL PROCEDURE

The experimental procedure used to process and characterize samples of compositions in the PG-PT and PG-PZT systems is illustrated by the flow chart shown in Figure 1. Amorphous compositions were prepared by either melting and rapidly quenching in a counter-rotating twin-steel-roller quenching apparatus, or by a solution (sol-gel) method. The melt-derived route was used to produce amorphous ribbon and ball-milled amorphous powder. The solution-derived method produced thin films by spin coating, and amorphous powder by gelling and drying the solution. The amorphous powders were then further processed with or without the addition of crystalline powders by pressing bulk samples, thick-film screen printing, or tape casting. Fillers were not added in the compositions presented in this paper. The five types of samples were heat treated to densify and/or crystallize the compositions, followed by characterization with x-ray diffraction, SEM, and electrical measurements. Additional details of the procedures used are described in References 20-23.

RESULTS AND DISCUSSION

Figure 2 illustrates the effect of crystal orientation on the dielectric constant and dissipation factor of pure $Pb_5Ge_3O_{11}$. The data for the nonoriented sample were measured on a pressed pellet of melt-derived powder fired at 700°C for two hours, while the data for the oriented sample were measured on a remelted (at 760°C) and crystallized (by cooling to 700°C and holding for 2 hours) melt-derived powder on gold foil (similar to the method used in references 3 and 4). The dielectric constant of the non-oriented polycrystalline ceramic sample ranges from ≈30 at 50°C to ≈80 at the Curie temperature. The dielectric constant of the oriented sample approaches that of a c-axis oriented single crystal. The variation in Curie temperature between the samples may be stress related.

The SEM micrograph in Figure 3 shows the c-axis orientation that occurs when remelting and crystallizing PG on a 96% alumina thick-film substrate. The x-ray diffraction pattern of the surface of this sample is shown in Figure 4, along with the pattern for nonoriented PG for comparison. The two main peaks of the oriented sample correspond to the (003) and (006) refections, indicating the high degree of c-axis orientation. A semi-quantitative relationship developed by Lotgering[24] was used to calculate a quality factor (F%) for the c-orientation from the XRD data as listed in Table 1. PG remelted and crystallized on alumina has a c-axis orientation of 60%. This orientation decreases to 17% on a thick-film Pt electrode on an alumina substrate.

Figure 5 shows the x-ray diffraction patterns of oriented and nonoriented PG·PT compositions. This composition has an equal molar percentage of PG and PT, however the volume ratio is ≈84/16 PG/PT. The XRD pattern of the nonoriented sample is of a crushed pellet of melt-derived amorphous powder sintered at 720°C for 20 hours. All of the peaks in this pattern correspond to either the ferroelectric PG ($Pb_5Ge_3O_{11}$) or PT ($PbTiO_3$) phases. With additions of PT or PZT to PG c-axis orientation still occurs in thick films, but is significantly reduced compared to pure PG (see Table 1). The opposite effect occurs in thin films as described below.

Figure 6 shows x-ray diffraction patterns of the surface of eight layers of PG sol-gel derived thin films spin-coated on a platinum coated silicon substrate fired at 500, 600, and 700°C for 30 minutes. The 500°C data illustrate that the PG phase does not fully develop until above this temperature. The 600 and 700°C patterns show c-axis oriented PG. The degree of orientation increases with increasing heat treatment temperature as shown by the orientation factors listed in Table 2. Also listed in this table are orientation factors for PG on borosilicate glass and thick-film platinum fired on alumina.

Thin films of PG with PZT additions resulted in a highly oriented PG phase. The PG·2PZT composition, corresponding to ≈70/30 volume ratio of PG to PZT, fired on platinum/silicon substrates showed c-axis orientations greater than 90% for firing temperatures of between 600 and 750°C, as listed in Table 2 with XRD patterns shown in Figure 7. This orientation is greater than any obtained with the PG composition. The PG (003) line appears to be shifting to a slightly lower d-spacing (higher 2θ) with increasing temperature, however this may actually be a transformation from an oriented metastable hexagonal 5-3 phase, represented by its (008) diffraction line, to the stable hexagonal 5-3 phase. The metastable (008) line is reported by Otto[25] to be located at d=3.63, while the (003) line of the stable phase is reported at d=3.56.[26] Experimental d-spacings for this line were determined to be 3.64 at 600°C and 3.57 at 750°C. The PG (006) line appears to show a similar shifting/transformation to a lower d-spacing.

SUMMARY

Solution-derived and melt-derived processing methods were used to prepare thin and thick-film, glass ribbon, tape cast, and bulk samples of compositions in the $Pb_5Ge_3O_{11}$- $PbZr_xTi_{1-x}O_3$ system. These compositions crystallize into multiple ferroelectric phases with low processing temperatures. Examples of processing techniques to produce c-axis orientation of PG were presented. The addition of PT or PZT to PG results in decreased c-axis orientation of the PG crystallites in thick-film samples, however significantly enhanced orientation occurs in thin-film form. The high PG compositions are being investigated for pyroelectric applications, while the high PT and PZT compositions are being studied for piezoelectrics with low processing temperatures. Additional details of the results of this research are described in references 20-23.

ACKNOWLEDGEMENTS

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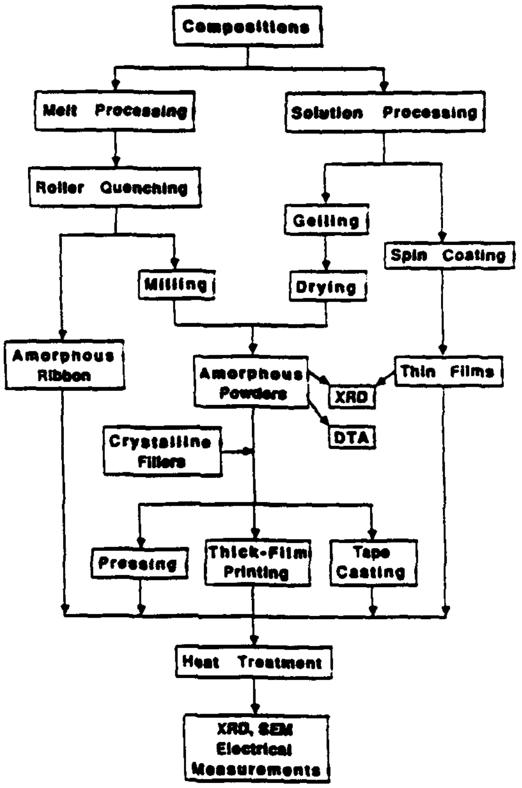

Figure 1 - Sample preparation and characterization procedure.

TABLE 1 - C-axis Orientation of Thick Films

Composition	Substrate	Orientation (F%)
PG	Al_2O_3	60
PG·PT	Al_2O_3	9
PG	Pt/Al_2O_3	17
3PG·PT	Pt/Al_2O_3	5
PG·PT	Pt/Al_2O_3	3
3PG·PZT	Pt/Al_2O_3	12
PG·PZT	Pt/Al_2O_3	4

TABLE 2 - C-axis Orientation of Thin Films

Thin Film Type	Temperature (°C)	Orientation (F%)
PG on Glass	500	41
	550	57
	600	59
PG on Pt/Al_2O_3	550	14
	600	17
	650	21
	700	20
PG on Pt/Si	550	11
	600	25
	650	33
	700	38
PG·2PZT on Pt/Si	600	>90
	650	>90
	700	>90
	750	>90

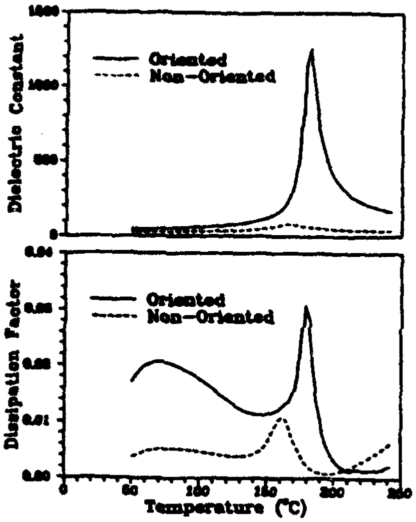

Figure 2 - Dielectric constant and dissipation factor plotted versus teperature for oriented and nonoriented PG.

Figure 3 - PG remelted and crystallized on an alumina substrate (800°C - 20 min., followed by 700°C - 1 hr.).

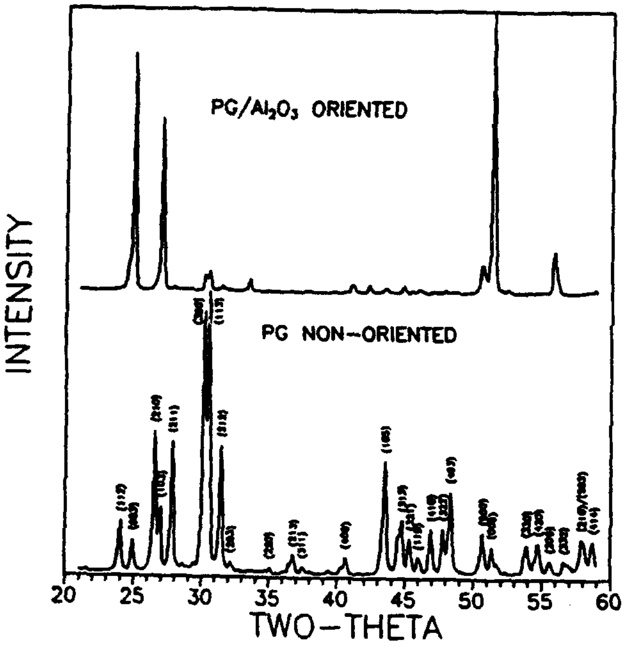

Figure 4 - X-ray diffraction patterns of oriented (thick film on an alumina substrate) and nonoriented PG.

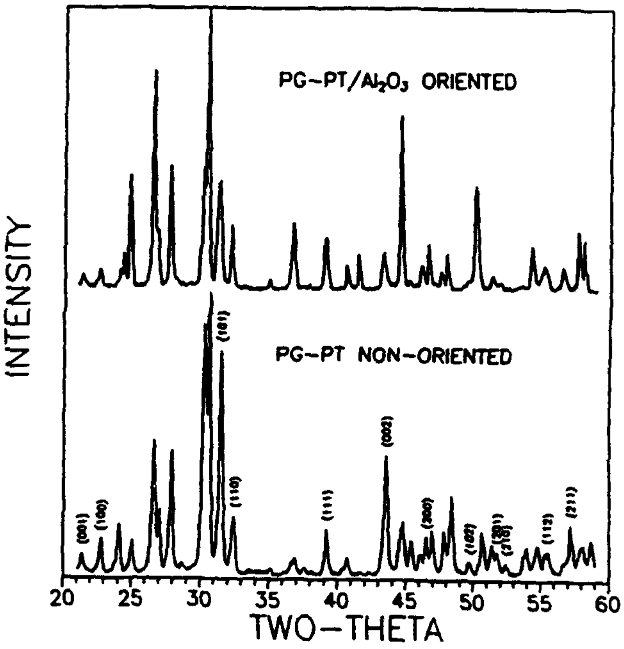

Figure 5 - X-ray diffraction patterns of oriented (thick film on an alumina substrate) and nonoriented PG·PT.

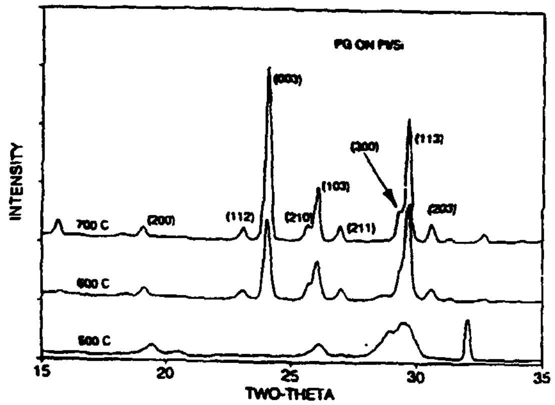

Figure 6 - X-ray diffraction patterns of $Pb_5Ge_3O_{11}$ thin films on Pt/Si substrates with 30 minute firing times.

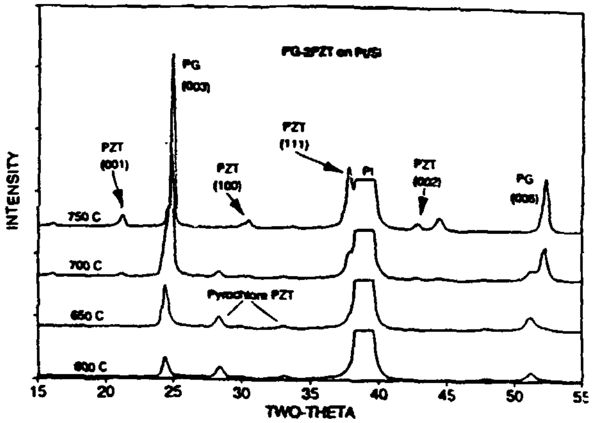

Figure 7 - X-ray diffraction patterns of $Pb_5Ge_3O_{11}\cdot 2PbZr_{0.5}Ti_{0.5}O_3$ thin films on Pt/Si substrates with 30 minute firing times.

APPENDIX 6

(Summary of Research Completed through August 1992)

FERROELECTRIC GLASS-CERAMICS BASED ON THE $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ SYSTEM*

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ABSTRACT

The crystallization behavior of amorphous compositions prepared from the $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) and $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ (PG-PZT) systems was investigated. Selected compositions were melted, quenched, and milled into powders. Pressed samples crystallize completely into multiple ferroelectric phases at 600°C (PG and PT, or PG and PZT), and densify to 95-99% of theoretical density at 700°C. The low softening temperatures (≈ 340°C) of these glasses, indicate the potential of densification at even lower temperatures. Ferroelectric hysteresis loops and electrical poling of the samples was not possible, however research is continuing to increase the crystallite size and orientation to produce useful piezoelectric and pyroelectric properties.

*Supported by the National Science Foundation and the Office of Naval Research.

I. INTRODUCTION

Ferroelectric glass-ceramics have been used in capacitor, electro-optic, and hybrid circuit applications for many years,[1] but useful piezoelectric and pyroelectric properties have not been developed. Typically a ferroelectric phase is crystallized in a nonferroelectric glass matrix, which causes electrical poling of the ferroelectric phase to be very difficult. In this research a new ferroelectric glass-ceramic system ($Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$) was investigated, where 100% of the composition can potentially crystallize into multiple ferroelectric phases.

$Pb_5Ge_3O_{11}$ is an unusual ferroelectric crystal, because it can be easily formed into a glass, due to the presence of the glass former GeO_2. The piezoelectric properties of $Pb_5Ge_3O_{11}$ are relatively low, however the pyroelectric properties are of interest for thermal detector applications. The excellent piezoelectric properties of compositions in the $Pb(Zr_xTi_{1-x})O_3$ solid solution system are well established, and have been extensively used for many years in a wide range of transducer applications. Thus, the PG-PZT system will potentially combine the glass forming ability of $Pb_5Ge_3O_{11}$ with the excellent properties of PT or PZT.

Ferroelectricity in $Pb_5Ge_3O_{11}$ was independently discovered by Iwasaki et al.[2] and by Nanamatsu et al.[3] in 1971 in single crystals prepared by the Czochralski and Bridgman methods, respectively. The existence of $Pb_5Ge_3O_{11}$ single crystals confirmed the PbO-GeO_2 phase diagram work reported by Sperankaya[4] in 1959. In a general way, the lead germanate literature can be divided into two types of research: cation substitutions; and the use of $Pb_5Ge_3O_{11}$ as a sintering aid. Cation substitutions to $Pb_5Ge_3O_{11}$ have been made to increase the room temperature dielectric constants by reducing the ferroelectric to paraelectric phase transition temperature (Curie temperature of $Pb_5Ge_3O_{11}$ is 177℃).[5-10]

In a second type of research, $Pb_5Ge_3O_{11}$, with a low melting point of 738℃, has been used as a sintering aid.[11-15] In this research up to thirty weight percent PG has been mixed with other crystalline ferroelectric compounds, such as PZT or PLZT, to lower the processing temperatures, and to increase the density of the final product. However, in all of the studies reported, a non-crystalline residual matrix has been left decreasing the electrical properties of the final material. Thus, from the literature review we have not found any references of the PG-PT-PZ system being melted and formed into a single glass.

In the next section the experimental procedure used to process and characterize PG-PT-PZ compositions will be described. In Section III density, DTA, x-ray diffraction, and electrical property results will be discussed, followed by a summary of this research and planned future work in Section IV.

II. EXPERIMENTAL PROCEDURE

Five compositions were prepared: $Pb_5Ge_3O_{11}$, $3Pb_5Ge_3O_{11}\cdot PbTiO_3$, $Pb_5Ge_3O_{11}\cdot PbTiO_3$, $Pb_5Ge_3O_{11}\cdot 3PbTiO_3$, and $Pb_5Ge_3O_{11}\cdot Pb(Zr_{1/2}Ti_{1/2})O_3$. Figure 1 shows the experimental procedure that was used to prepare and characterize samples of these compositions. The starting materials were reagent grade Pb_3O_4, TiO_2, and ZrO_2; and electronic grade GeO_2. Pb_3O_4 was chosen as a starting material instead PbO to reduce the possibility of reduction to metallic lead and subsequent reaction with the platinum crucible. Pb_3O_4 converts to PbO at about 525°C supplying extra oxygen to the system (see DTA and TGA results in Figure 2).

The batches were mixed in either distilled water or methanol for five hours, dried at 100°C for twenty hours, and transferred to a platinum crucible for melting. The crucible was placed directly into the furnace at temperatures from 850 and 1100°C depending on composition with a hold time of fifteen minutes. The molten liquid was poured into distilled water maintained at 2°C. The glass obtained by this quenching method was then ball milled in distilled water for twenty hours. After ball milling the slurry was screened through a 325 mesh (45 μm) sieve, and dried at 100°C. DTA and x-ray diffraction were conducted on the glass powders. Pellets 13 mm in diameter and 1-2 mm thick were pressed without binder at a pressure of 10,000 psi held for one minute. After heat treatments at a several temperatures and times, the samples were analyzed with x-ray diffraction and SEM. Samples were also polished and electroded with sputtered gold followed by a layer of air-dried silver paint for electrical property measurements.

III. RESULTS AND DISCUSSION

Samples of the quenched glasses before ball milling were ground in a mortar and pestle. X-ray diffraction patterns of these powders are shown in Figure 3. The $Pb_5Ge_3O_{11}$ composition is x-ray amorphous without crystalline peaks. The other four compositions with additions of $PbTiO_3$ or $Pb(Zr_{1/2}Ti_{1/2})O_3$ are mostly amorphous, but have small crystalline peaks

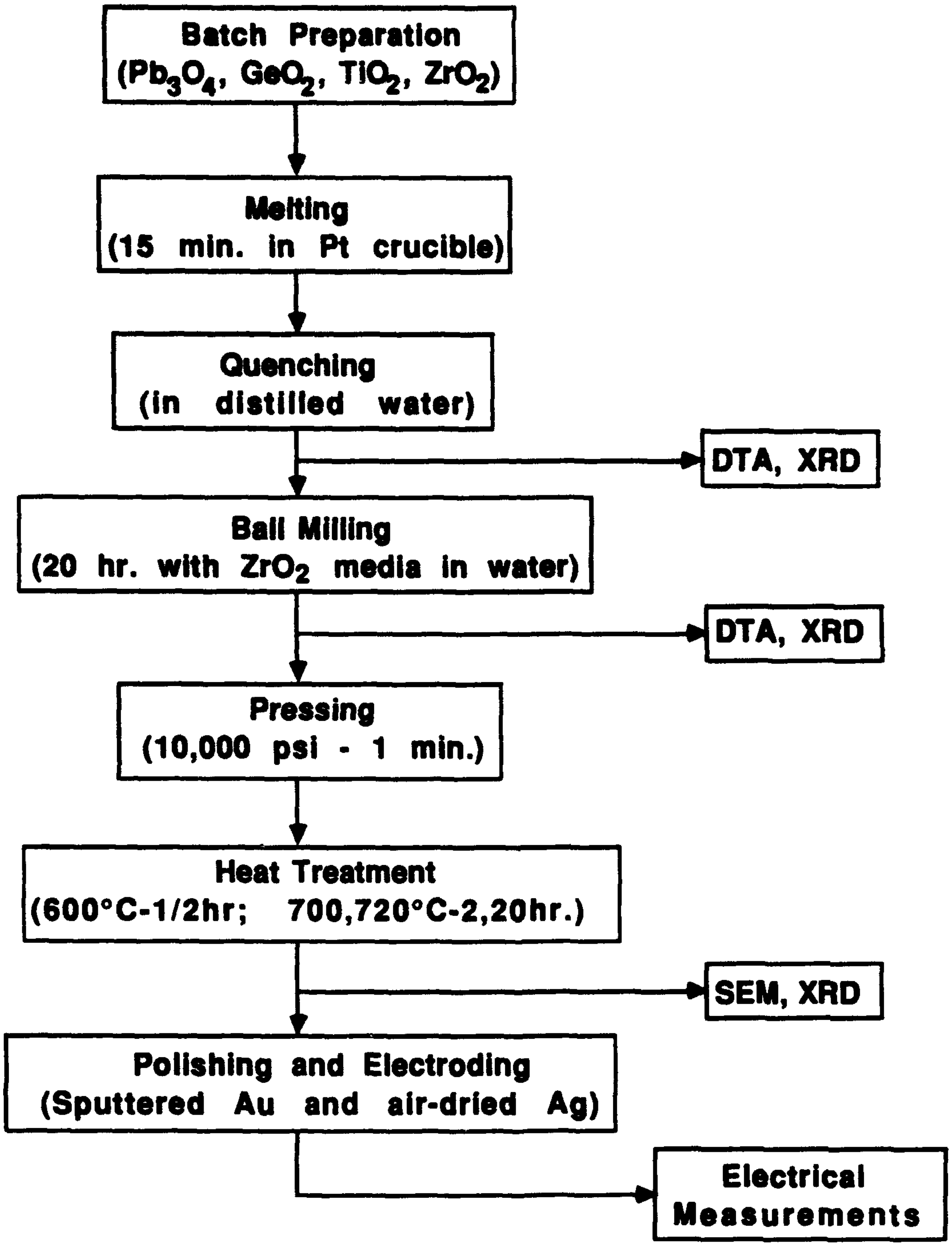

Figure 1 - Flow chart of the experimental procedure used for sample preparation and characterization.

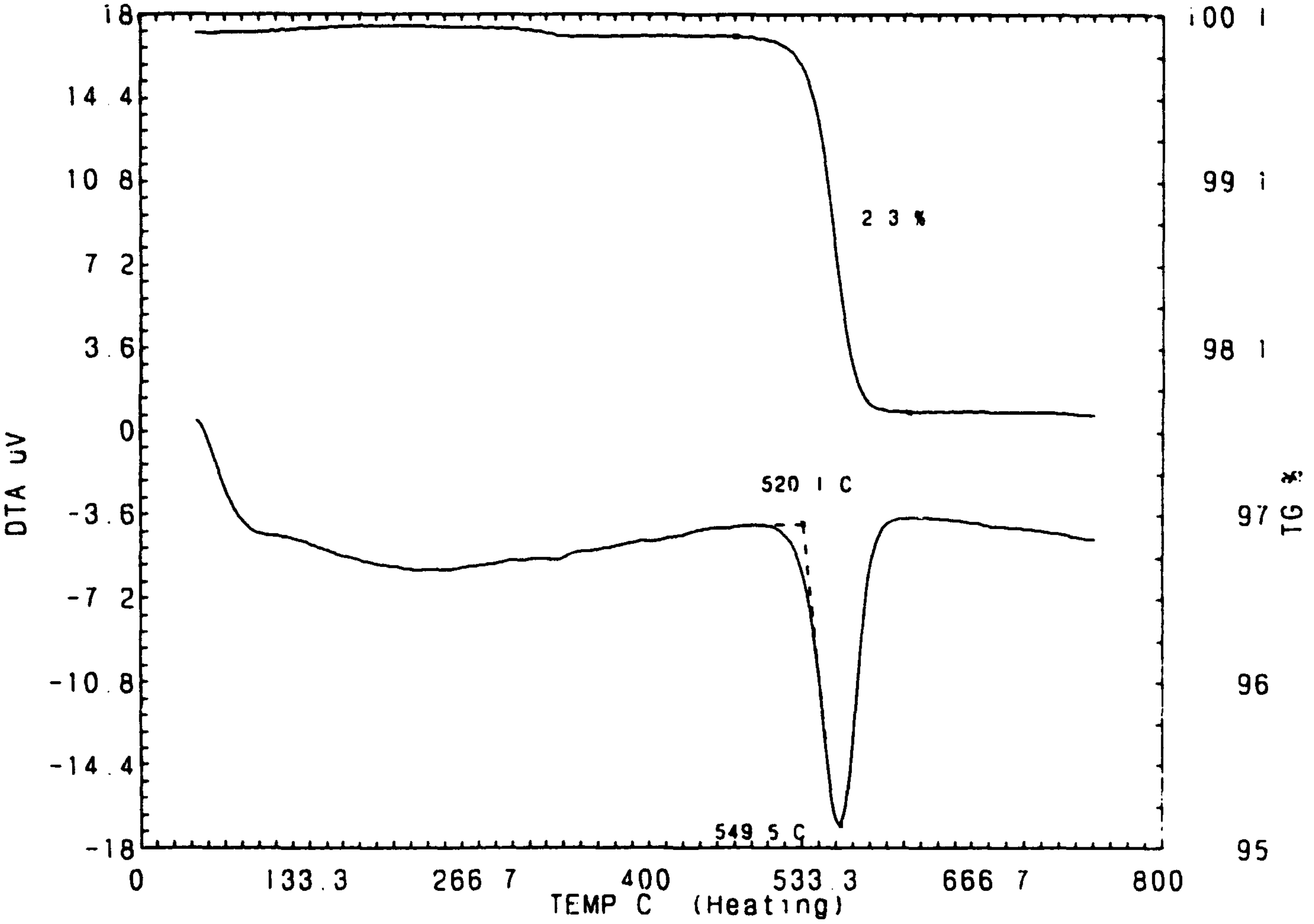

Figure 2 - DTA (lower curve) and TGA (upper curve) profiles of Pb_3O_4. The endothermic peak in the DTA curve at 525°C occurs because of the reduction of Pb_3O_4 to PbO, with the corresponding weight loss shown in the TGA curve.

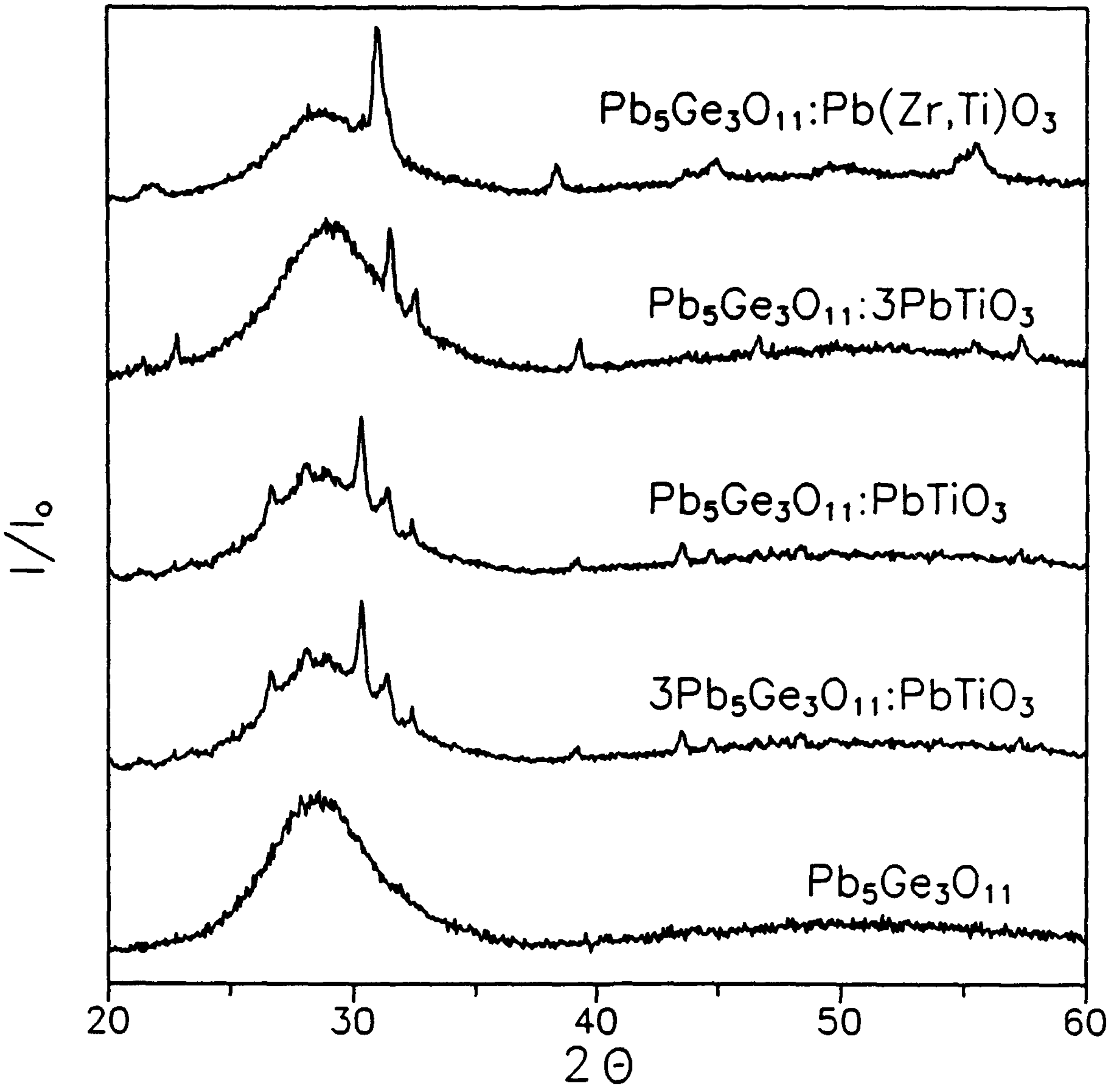

Figure 3 - X-ray diffraction patterns of the as-quenched glasses (before ball milling).

corresponding to the desired ferroelectric phases $Pb_5Ge_3O_{11}$, $PbTiO_3$, and/or $Pb(Zr_{1/2}Ti_{1/2})O_3$. These results indicate that quenching in water produces a fast enough quenching rate for the pure $Pb_5Ge_3O_{11}$ composition, but not quite fast enough for the other compositions. Inspection of the quenched glass showed that the smaller particles appeared amorphous, while the larger particles (with slower cooling rates) were partially crystalline.

Differential Thermal Analysis (DTA) was run on these same powders (except for the $Pb_5Ge_3O_{11}\cdot 3PbTiO_3$ composition) as shown in Figure 4. At temperatures from 334 to 347°C endothermic shifts occur in the baseline corresponding to the softening and densification of the glass powders. The degree of densification is controlled by the amount of crystalline material present, and the separation between the softening and crystallization processes. Large exothermic peaks occur because of crystallization with peak temperatures of 394 to 412°C. If the onset of the crystallization occurs before densification from glass softening is complete, then the viscosity will increase significantly limiting the densification in this temperature range. Higher temperatures where the crystalline material will densify would then be necessary to densify the compositions. The DTA curve for pure PG shows a clear separation of the softening and crystallization temperature ranges, and thus should densify at very low temperatures (< 350°C). The separation between the softening and crystallization in the other compositions is less clear, probably because of the crystalline material present in the initial glass. Eliminating this crystalline material with faster quenching rates will be needed to clarify this.

In the pure PG composition the first crystallization peak shown in Figure 4 at 394°C corresponds to the crystallization of a metastable nonferroelectric $Pb_5Ge_3O_{11}$ phase.[16] A small second exothermic peak occurs at 499°C where the metastable phase transforms to the stable ferroelectric $Pb_5Ge_3O_{11}$ phase. Thus, based on the DTA results the pure PG glass powder should densify completely and crystallize to the ferroelectric phase with heat treatment at 500°C. The other compositions crystallize the $Pb_5Ge_3O_{11}$, $PbTiO_3$ and/or $Pb(Zr_{1/2}Ti_{1/2})O_3$ phases based on x-ray diffraction results shown later in this section. Large and small exothermic peaks also occur in these compositions, however the details of when the phases crystallize have not yet been determined (x-ray diffraction has only been run on samples heat treated at 600°C or higher).

Figure 4 also shows the melting of the compositions by the large endothermic peaks at around 740°C. With the addition of PT or PZT to PG this temperature slightly decreases. The PG·PZT composition (labeled 2PG:PT:PZ) also shows a small endothermic peak at 703°C, presumably because of the melting of a minor phase that is present. On cooling similar behavior

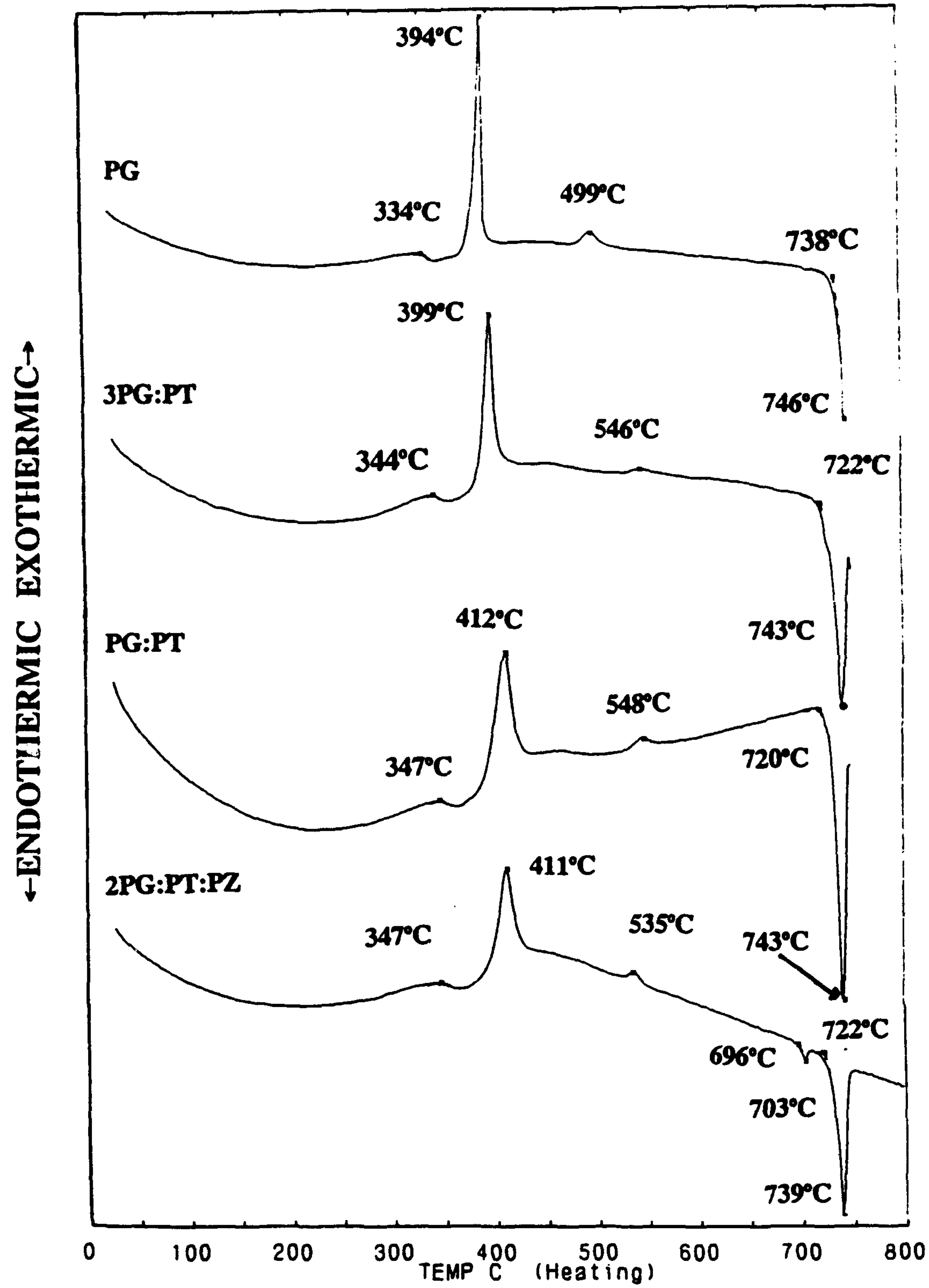

Figure 4 - DTA patterns on heating the as-quenched glasses (before ball milling) at 10°C/minute.

occurs as shown in Figure 5, where the PG·PZT composition exhibits a large exothermic peak from recrystallization followed by a second small peak. The other compositions have large single crystallization peaks, however the pure PG composition appears to possibly have a very small peak at 676°C. This may be caused by having compositions that are slightly off stoichiometry.

The PG·PT composition also shows a small exothermic peak at 469°C. This is believed to be a result of the latent heat of the discontinuous first order paraelectric to ferroelectric phase transition of $PbTiO_3$. A similar peak is not apparent in the 3PG·PT composition, probably because of the smaller amount of PT (only 25%). The PG·PZT composition would not be expected to have a peak corresponding to the paraelectric to ferroelectric transition of PZT, because this PZT composition undergoes a continuous second order transition which does not have a latent heat.[17] $Pb_5Ge_3O_{11}$ transforms from a paraelectric to ferroelectric phase at 177°C, however this transition is also second order, and thus a latent heat would not occur.

The softening temperatures from the DTA data are plotted versus composition in Figure 6, showing the small increase with the addition of PT to PG. A data point is also plotted for the PG·PZT composition showing that the addition of PZT does not significantly affect the softening temperature. Part of a preliminary phase diagram of the PG-PT and PG-PZT systems, based on the DTA data and observations of melts at various temperatures, is also plotted in Figure 6. The data indicate that there is a eutectic point that occurs very close to the PG composition with a broad liquid plus solid region towards PT or PZT. Additional data will be needed to more accurately construct these phase diagrams.

The results presented thus far have been on the quenched glass compositions before ball milling that were ground in a mortar and pestle. An interesting result occurred from ball milling these compositions in distilled water. Figure 7 shows x-ray diffraction patterns of the as-quenched PG composition, and after ball milling in methanol and water. The glass ball milled in water crystallizes a phase that does not appear to match any of the JCPDS x-ray diffraction cards. A similar pattern was also found to occur after ball milling the other compositions (with PT and PZT additions) in water. Additional studies show that this unidentified phase crystallizes from contact with water at room temperature without ball milling.

The x-ray diffraction pattern shown in Figure 7 for the PG glass ball milled in methanol also shows the present of a crystalline phase. However, these peaks correspond to the

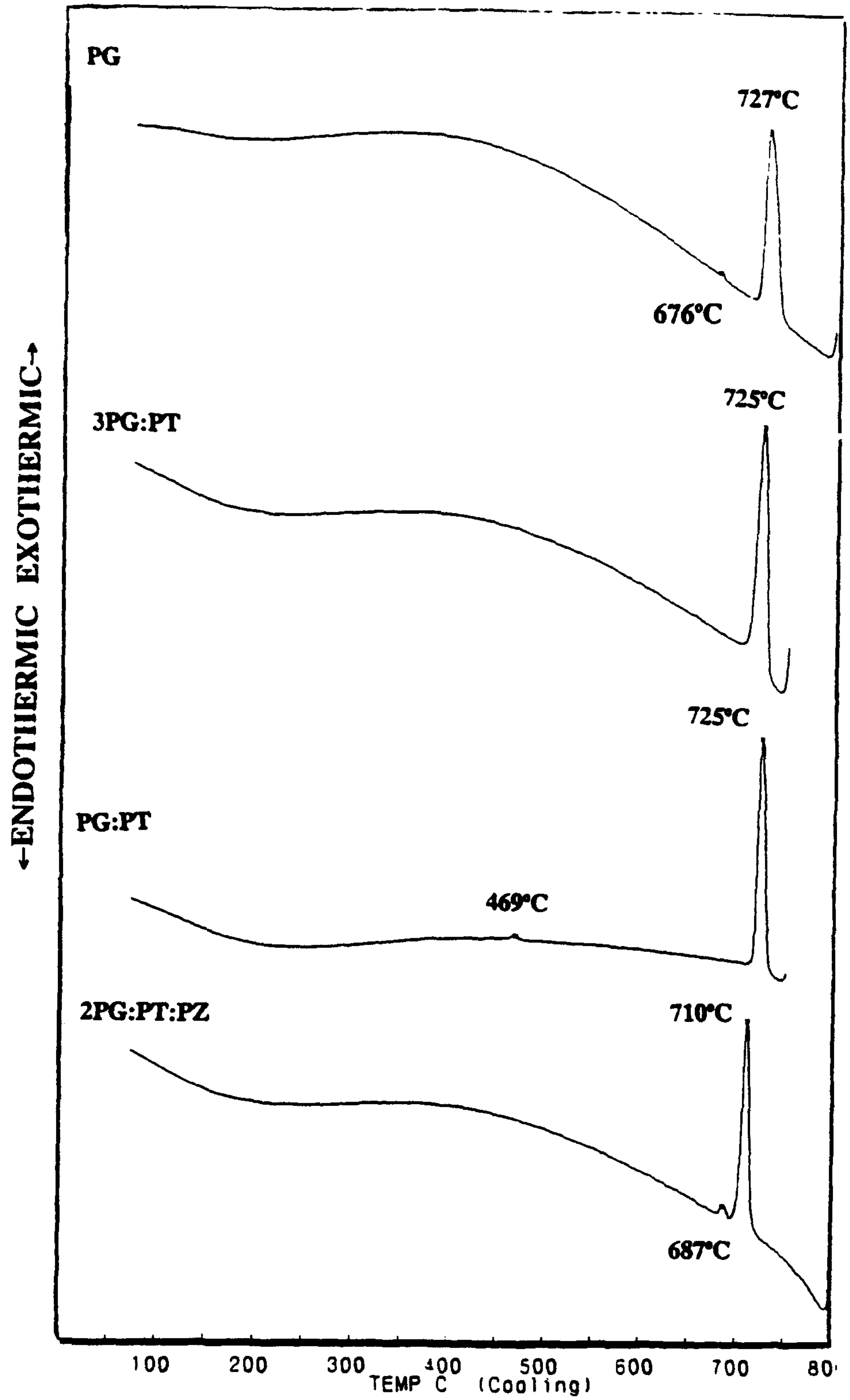

Figure 5 - DTA patterns on cooling the as-quenched glasses (before ball milling) at -10°C/minute.

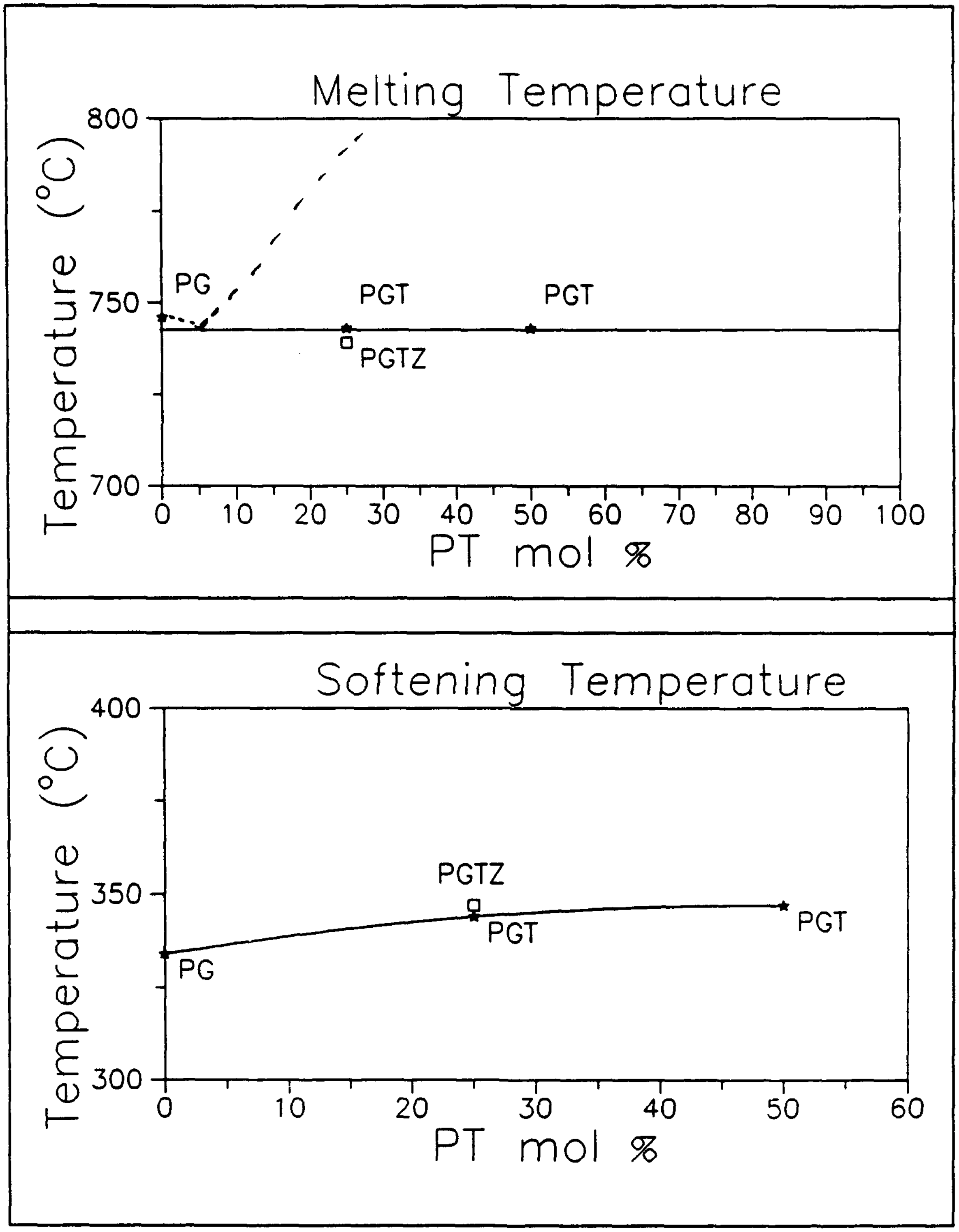

Figure 6 - Preliminary phase diagrams of the PG-PT and PG-PZT systems (upper figure). Softening temperature plotted versus the mole percent PT or PZT (lower figure).

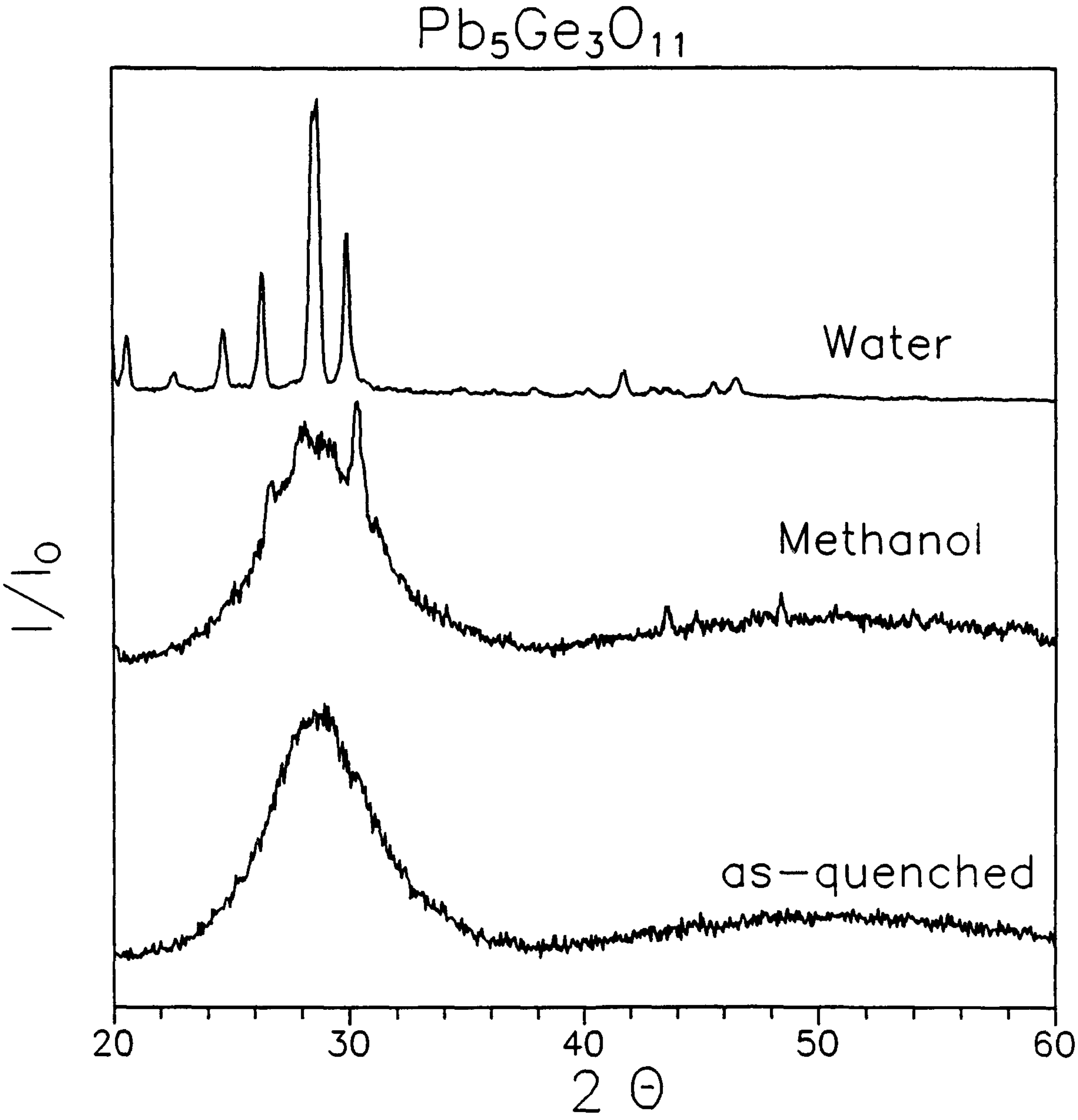

Figure 7 - X-ray diffraction patterns of the pure lead germanate composition after quenching and after ball milling in methanol and distilled water.

$Pb_5Ge_3O_{11}$ phase, and we believe that this did not crystallize from the ball milling in methanol, but instead is due to material that crystallized during quenching. Additional studies are planned to confirm this.

Pressed pellets of the glass powders that were ball milled in water and methanol were heat treated at various temperatures and times. The glass powders that were ball milled in methanol did not densify well, while the water ball milled powders did densify to 95-98% of theoretical density. The methanol may be affecting the surface of the glass powder in some way that adversely affects the densification behavior of the material. Water crystallizes the glass, and thus this powder does not densify from the softening of the glass powder, but does densify at higher temperatures (≈700-720°C) just below the melting point.

The unidentified phase transforms to the stable ferroelectric $Pb_5Ge_3O_{11}$ phase at or below 600°C. Figure 8 shows the x-ray diffraction patterns of the PG composition (ball milled in water) after heat treatments from 600-720°C with hold times from 1/2 to 20 hours. All of the peaks correspond to the ferroelectric $Pb_5Ge_3O_{11}$ phase, and no significant change occurs in the patterns as a function of heat treatment, indicating that the PG phase is fully developed below 600°C.

Figure 9 shows the x-ray diffraction patterns of the PG, 3PG·PT, PG·PT, and PG·PZT compositions (ball milled in water) after heat treatment at 720°C for 20 hours. As discussed above the peaks in the PG pattern correspond to the ferroelectric $Pb_5Ge_3O_{11}$ phase. Comparison of this pattern with the other three reveals additional peaks from the tetragonal $PbTiO_3$ phase in the 3PG·PT and PG·PT compositions, and from the perovskite (rhombohedral and/or tetragonal) PZT phase in the PG·PZT composition. The PT and PZT peaks are labeled with the hkl's on the 3PG·PT and PG·PZT patterns. In addition, a few small unidentified peaks occur in the PG·PZT composition.

The dielectric constants and dissipation factors at 1 MHz of samples heat treated at 700°C for two hours are plotted in Figures 10 and 11 versus temperature. The dielectric constants form a peak because of the ferroelectric to paraelectric phase transition of the $Pb_5Ge_3O_{11}$ phase. The dielectric constant increases at low temperatures as the PT content is increased, because of the higher dielectric constant contribution from the ferroelectric $PbTiO_3$ phase. The even higher dielectric constant of the PG-PZT composition indicates that the PZT phase is in the ferroelectric state. The dissipation factor of the four compositions also forms a peak at the PG transition. With PT addition the D.F. increases significantly at higher temperatures because of increased conduction

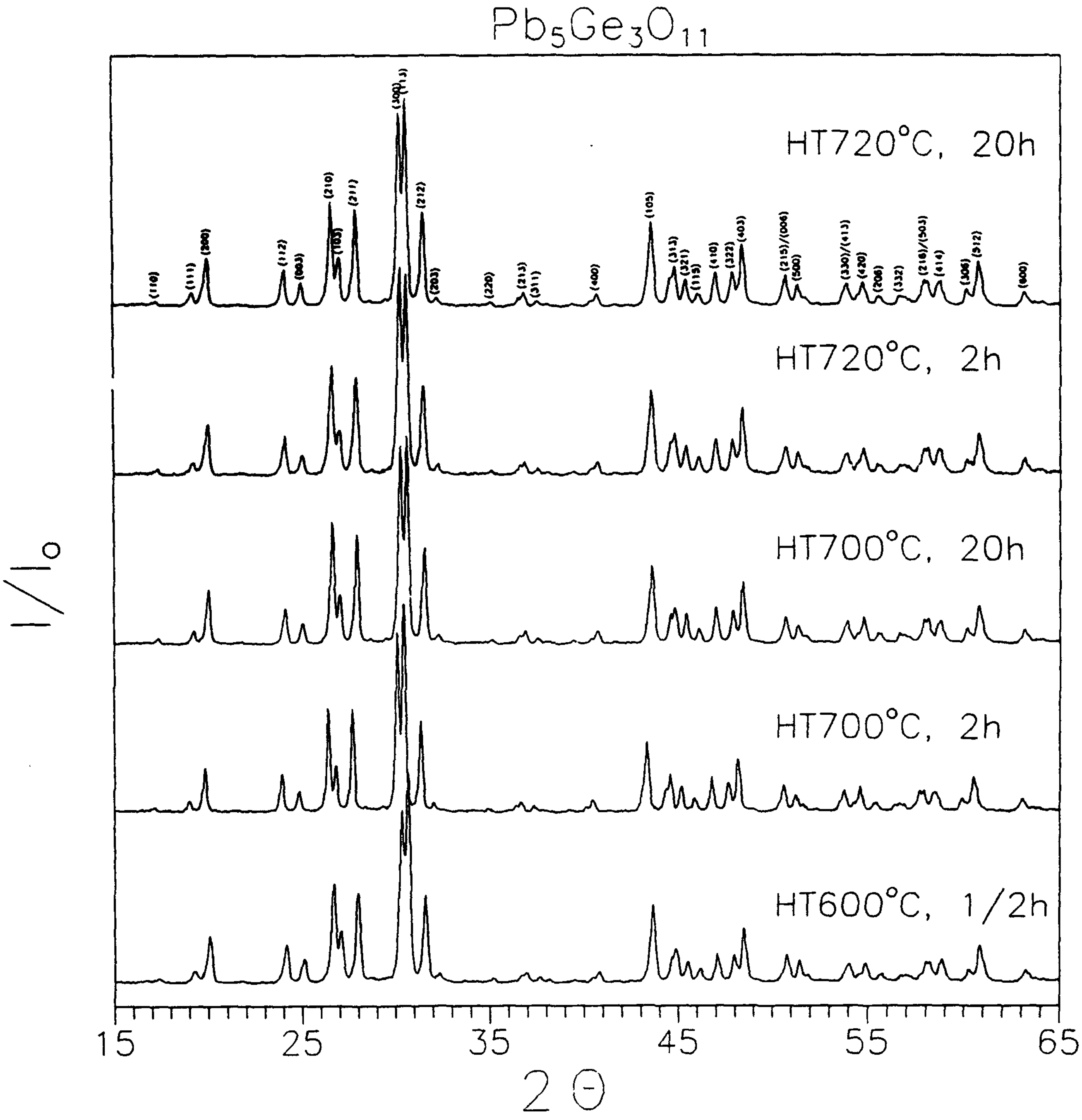

Figure 8 - X-ray diffraction patterns of the pure lead germanate composition heat-treated at different temperatures and times.

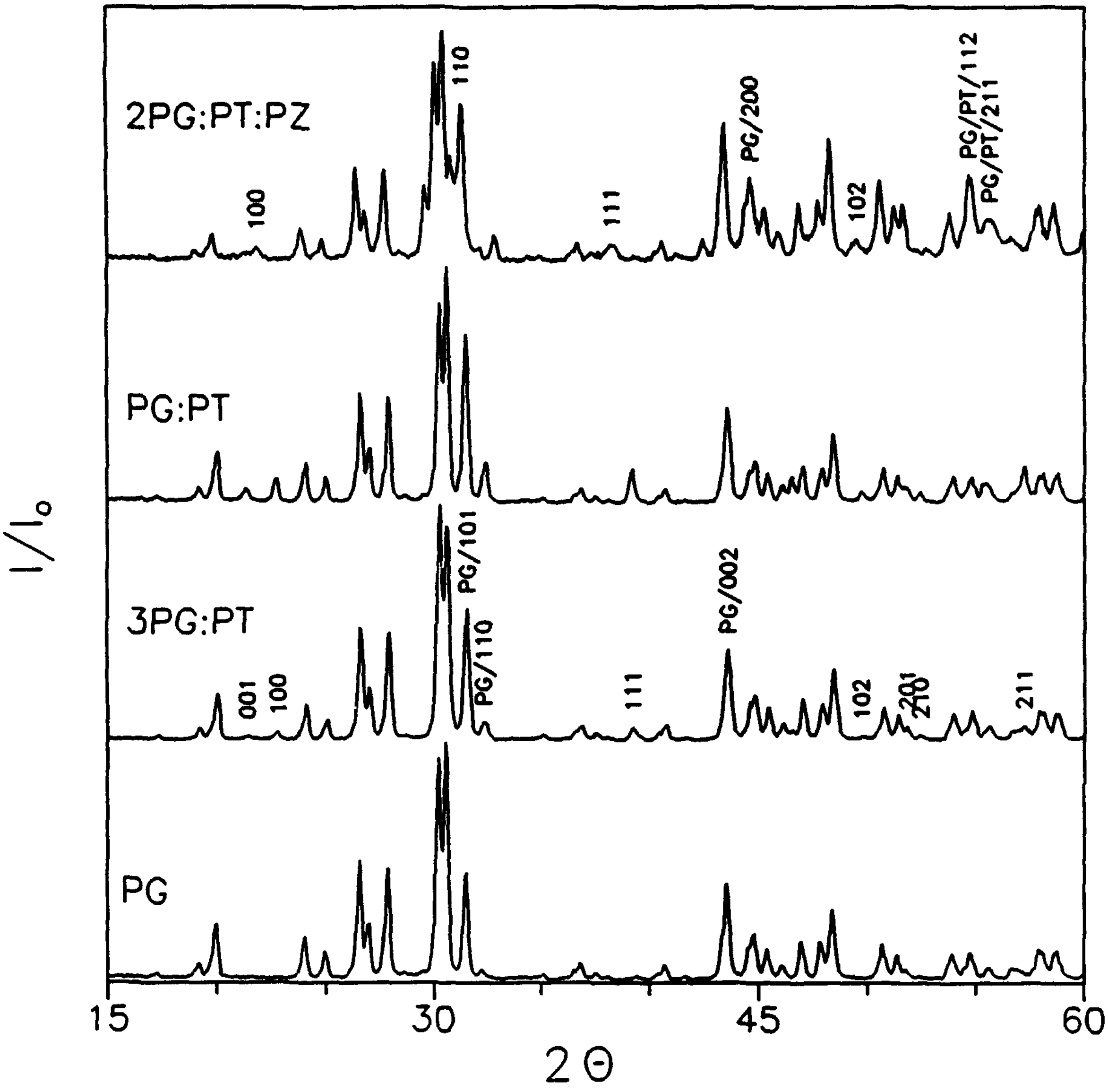

Figure 9 - X-ray diffraction patterns of four compositions after heat-treatment at 720°C for twenty hours. The $PbTiO_3$ and $Pb(Zr_{1/2}Ti_{1/2})O_3$ peaks of the 3PG·PT and 2PG·PZ·PT (same as PG·PZT) patterns are labeled with hkl's. The others peaks correspond to the ferroelectric $Pb_5Ge_3O_{11}$ phase. PG is labeled where peak overlap occurs.

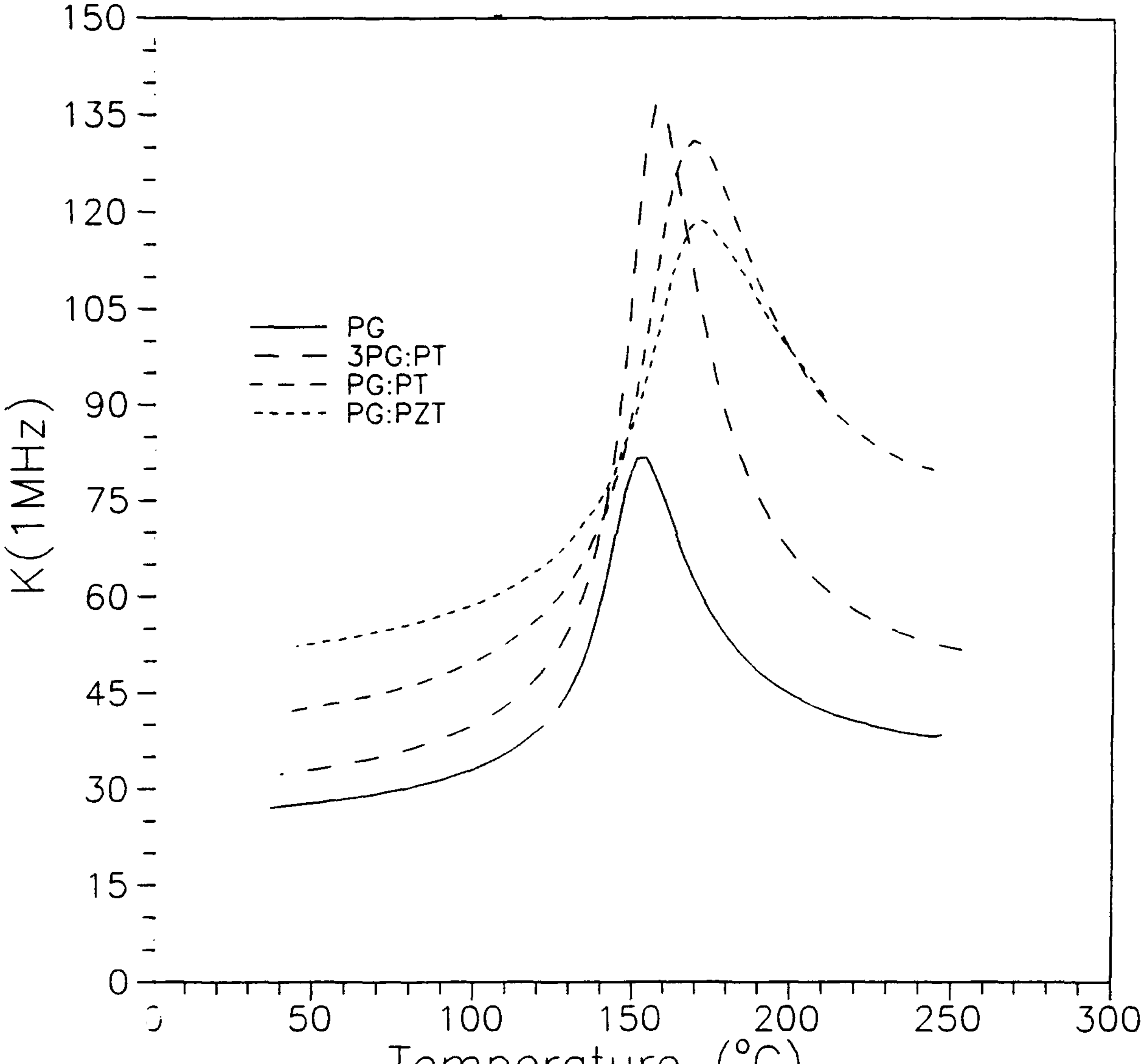

Figure 10 - The dielectric constant at 1 MHz plotted versus temperature.

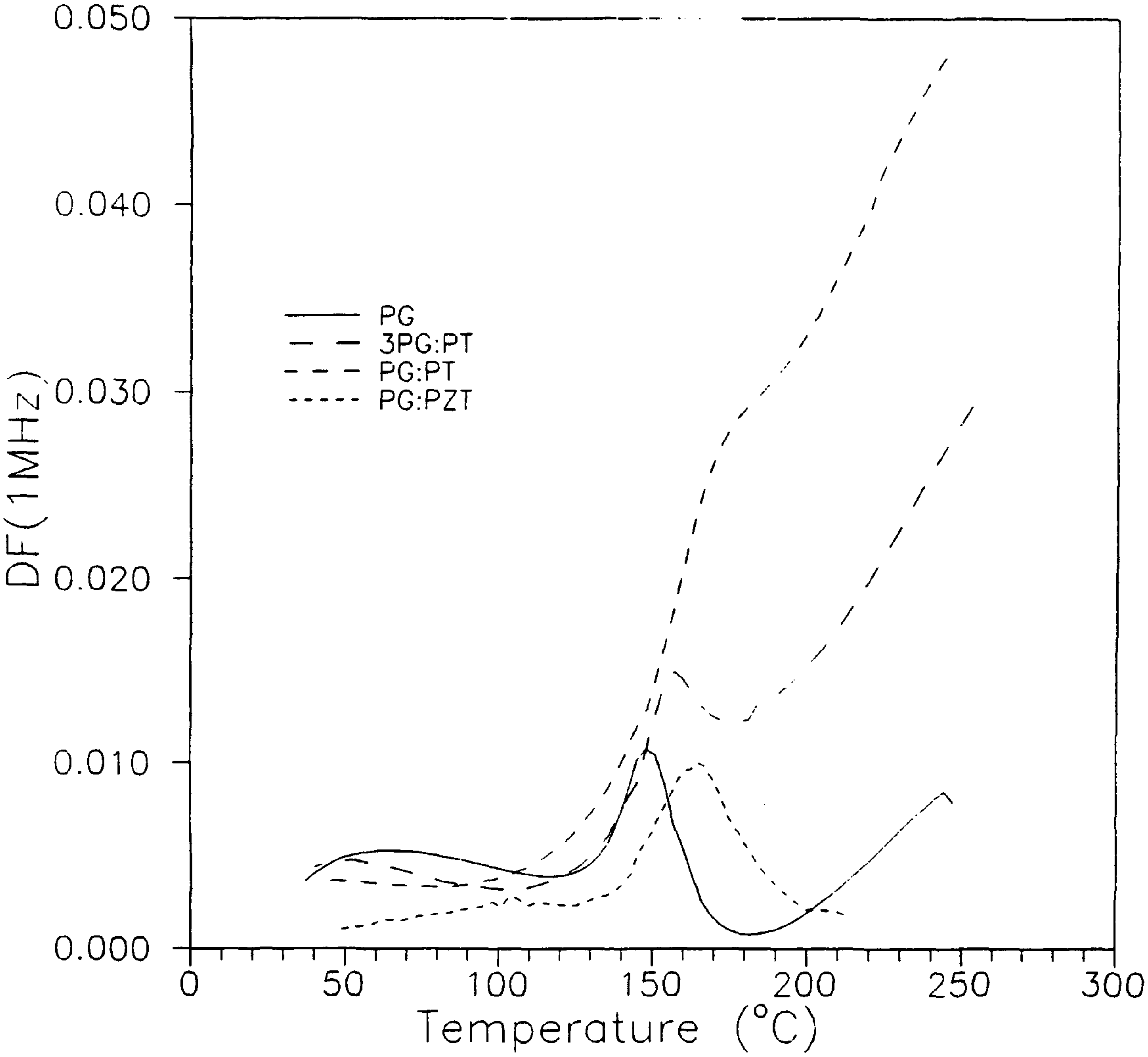

Figure 11 - The dissipation factor at 1 MHz plotted versus temperature.

losses, which is not seen with the addition of PZT.

Hysteresis loops and electrical poling of the samples were not achieved with electric fields up to 30 KV/cm. The measurement of the piezoelectric d_{33} coefficient was used to evaluate the degree of electrical poling (zero values were measured). SEM micrographs of the samples showed good densification, however individual crystallites were not observable. These results suggest that the ferroelectric crystallites are very small and thus single domain, which would cause the orientation to be difficult. The samples may also contain a residual glass matrix which would also increase the coercive field.

IV. SUMMARY

Compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ system were melted and prepared into powders. Some crystallization occurred depending on composition and quenching conditions. Reaction with water was found to crystallize an unidentified phase in all compositions, which transformed to the desired ferroelectric phases during heat treatment. The compositions densified to 95-98% of theoretical density at 700-720°C. The low softening temperatures of these glasses (<350°C) indicate the potential of densification at even lower temperatures. Ferroelectric hysteresis loops and electrical poling of the samples were not possible, however research is continuing to increase the crystallite size and orientation to produce useful piezoelectric and pyroelectric properties.

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APPENDIX 7

Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part I: The $Pb_5Ge_3O_{11}$-$PbTiO_3$ System

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ABSTRACT

Melt derived amorphous compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) system were prepared by water and roller quenching methods. The crystallization behavior of this system was investigated by Differential Thermal Analysis (DTA), powder x-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The glass softening and crystallization temperatures were found to increase as the PG/PT ratio decreases. A solidus line on the PG-PT phase diagram occurs at 725±6°C with a eutectic point near the PG composition. Pressed glass powder samples crystallize into a diphasic PG and PT ferroelectric material by 600°C , and densify to 93-99% of theoretical density between 700-720°C.

I. INTRODUCTION.

The crystallization of glasses is utilized to produce glass-ceramics for a wide variety of applications [1]. The crystallization behavior and control of the microstructure of glass-ceramics has been thoroughly studied in many systems, resulting in the development of compositional modification and processing techniques to control the nucleation and crystal growth [1].

The study of ferroelectric glass-ceramics began in the early 1960's [2]. Subsequently, the crystallization of a variety of ferroelectric phases, such as $BaTiO_3$ [3-6], $PbTiO_3$ [7-20], and $NaNbO_3$ [6,21-24] have been investigated. However, in all of the glass-ceramic compositions described above either a glass former, in addition to the ferroelectric crystalline phase constituents, was required to form the stable starting glasses, or extremely rapid quenching techniques were necessary when the glass former content was reduced or eliminated. These types of processing techniques have some disadvantages. First, in compositions with glass former additions, upon heating the glass to crystallize the desired ferroelectric phase either a non-ferroelectric crystalline residual matrix results, or a nonferroelectric glass matrix is left in the sample. As a consequence, the ferroelectric properties are lowered, and the performance of the material diminished. Second, in compositions that do not contain glass former constituents, rapid quenching techniques are necessary to form glasses. The temperatures used to crystallize the ferroelectric phases are usually low, however compact powders do not sinter from softening of the glass, and thus temperatures above 900°C (see Ref.[4]) are required for densification. This limits the type of electrode that can be used in cofiring, and the volatility of certain components increases, such as PbO which complicates the processing.

Ferroelectricity in $Pb_5Ge_3O_{11}$ was independently discovered by Iwasaki et al. [25], and by Nanamatsu et al. [26] in 1971 in single crystals prepared by the Czochralski and Bridgman methods, respectively. At the Curie point of 177°C a slight distortion occurs from a paraelectric hexagonal structure to a ferroelectric trigonal structure. The spontaneous polarization develops along the c-axis of the trigonal crystal where only 180° domains are possible [27]. The piezoelectric properties of PG are relatively low, however the pyroelectric properties are of interest for thermal detector applications [28].

Another unique property of PG is that it can be easily formed into a glass, due to the presence of the glass former GeO_2. Thus, by combining the glass formability of PG with the excellent properties of a well known ferroelectric (such as lead titanate), unique combinations of ferroelectric phases may result. In this research a new ferroelectric glass-ceramic system, $Pb_5Ge_3O_{11}$-$PbTiO_3$, was investigated. Compositions in this system crystallize into multiple ferroelectric phases at 600°C, and densify to 93-99% (depending on PG/PT ratio) of the theoretical density at 700-720°C.

Relatively low processing temperatures have been achieved in crystalline forms of lead germanate based materials [29-35], and have been previously reviewed [36-37].

II. EXPERIMENTAL PROCEDURE.

Four different compositions, PG, 3PG·PT, PG·PT, and PG·3PT were prepared from reagent grade Pb_3O_4, TiO_2, and electronic grade GeO_2. Pb_3O_4 was chosen as a starting material instead of PbO to reduce the possibility of reduction to metallic lead and subsequent reaction with the platinum crucible. TGA and DTA results show that red lead oxide (Pb_3O_4) transforms to yellow lead oxide (PbO) at about 520°C supplying extra oxygen to the system (Figure 1).

The batches were mixed either dry or in distilled water for five hours. The wet mixed powders were dried at 100°C for 20-24 hours before melting. The dry mixed powders were transferred to a platinum crucible directly after mixing for melting. The crucible was covered with a Pt-lid and placed into the furnace at temperatures from 800 to 1275°C, depending on composition with a hold time of 15-20 minutes. A lead source was introduced in the furnace when compositions where melted above 900°C. The molten liquid was poured either into distilled water at $\approx$2°C or into a twin-roller quenching apparatus to produce glass ribbon. The glass obtained by these quenching methods was then ball milled with zirconia media in a nalgene jar in either a liquid medium (distilled water or methanol) or dry for twenty hours. DTA and XRD were conducted on powder before and after the ball milling process. After ball milling, the slurry was screened through a 325 mesh (45 μm) sieve, and dried at 100°C. The dry milled powders were screened through a 200 mesh (75 μm) sieve. Pellets 13 mm in diameter and 1-2 mm thick were pressed without binder at a pressure of 10 ksi for one minute. After heat treatments at several temperatures and times, the samples were analyzed with XRD and SEM.

III. RESULTS AND DISCUSSION.

XRD patterns of the water and roller quenched glass powders are shown in Figures 2 and 3, respectively. A comparison between these two figures shows that extremely rapid quenching techniques are not necessarily needed to produce amorphous (or nearly amorphous) PG-PT compositions. However, the roller quenching technique offers some advantages over water quenching techniques, such as the preparation of thin dense glass ribbon. Only the $Pb_5Ge_3O_{11}$, and $3Pb_5Ge_3O_{11} \cdot PbTiO_3$ compositions were completely x-ray amorphous (Figure 3). The other two compositions with further additions of PT were mostly amorphous, but have small crystalline peaks corresponding to one of the desired ferroelectric phases, i.e. PT. The lead titanate phase appears to have crystallized during transfer of the platinum crucible to the quenching systems. Potentially the quenching procedure could be further optimized to avoid crystallization completely.

Differential Thermal Analysis (DTA) was measured at 10°C/min in a flowing nitrogen atmosphere for both water quenched [38] and roller quenched [39] glass powders which were prepared by dry grinding with a mortar and pestle. The results obtained were very similar indicating that the small differences in the amounts of crystalline phases present did not significantly affect the softening and crystallization processes. Figure 4 shows the DTA patterns of the roller quenched glass powders of the system PG-PT upon heating. Endothermic shifts occur in the baseline corresponding to the softening and densification of the glass powders. These shifts occur at temperatures from 333 to 407°C, with increasing temperature as the PT content is increased. The degree of densification at the transition or softening temperature is controlled by the amount of crystalline material present, and the separation between the softening and crystallization processes. The first exothermic crystallization peaks occur at temperatures from 385 to 473°C. If the onset of the crystallization occurs before densification from glass softening is complete, then the viscosity will increase significantly limiting the densification in this temperature range. Higher temperatures, where the crystalline material will densify, would then be necessary to densify the compositions. The DTA curves in Figure 4 show a separation of the softening and crystallization temperature ranges indicating the potential of densification at very low temperatures (< 407°C).

In the pure PG composition the first crystallization peak at 385°C corresponds to the crystallization of a metastable nonferroelectric $Pb_5Ge_3O_{11}$ phase [40]. A small second exothermic peak occurs at 495°C, where the metastable phase transforms very rapidly to the stable ferroelectric PG phase [40].

Figure 4 also shows that large endothermic peaks occurs at around 740°C, and they slightly decrease as the PG/PT ratio decreases from 746 to 738°C. On cooling the PG-PT compositions (see Figure 5), the DTA exhibit a large exothermic peak from recrystallization ranging from 715 to 703°C. This hysteretic behavior of the DTA measurements indicates the presence of superheating and supercooling. Furthermore, these results suggest that a solidus line occurs in the PG-PT phase diagram around 725±6°C, and a eutectic point occurs very close to the PG composition with a broad liquid plus solid region towards PT.

In Figure 5 a small exothermic peak occurs at lower temperatures around 475°C in the higher PT compositions. This is believed to be a result of the latent heat of the discontinuous first order paraelectric to ferroelectric phase transition of $PbTiO_3$. As mentioned before, $Pb_5Ge_3O_{11}$ transforms from a paraelectric to ferroelectric phase at 177°C, however this transition is second order [41] and thus a latent heat would not occur at that temperature.

Pressed pellets of the glass powders that were ball milled in water densify to 93-99% of theoretical density at 700-720°C, and crystallize completely, within the limits of x-ray diffraction, into the desired phases by 600°C. Figure 6 shows the density of pressed pellets of water ball milled PG-PT glass powders as a function of heat treatment temperature. All samples were heat treated for 2 hours at the specified temperature, except those heat treated at 600°C which were held for 1/2 hour. Water ball milled powders were found to crystallize an unknown metastable phase at room temperature [42], which transforms to the desired ferroelectric phases during heat treatment. This metastable crystalline phase prevents densification from the softening of the glass. However, at higher temperatures from 600 to 700°C a rapid increase in density occurs, reaching a maximum between 700-720°C. Increasing the temperature to 740°C was found to decrease the density. As shown in Figure 4, the pure PG composition has an onset of melting at 736°C, reaching the peak melting temperature at 746°C. At 740°C the PG composition is partially melted, while the other compositions with PT are in a solid plus liquid phase region. It is believed that at this temperature only the small particles in the system are melted, forming holes in the structure and increasing the porosity of the material, resulting in a decrease in density. This increase in porosity has been corroborated by SEM studies of fractured surfaces. The partial melting of the samples at 740°C resulted in large well defined PG and PT crystallites, as shown in Figure 7.

X-ray diffraction patterns of the PG and PG·PT compositions heat treated at different times and temperatures are shown in Figures 8 and 9. All of the XRD peaks in Figure 8 correspond to the ferroelectric PG phase, and no significant change occurs as a function of heat treatment temperature from 600 to 720°C, and hold times from 1/2 to 20 hours. Figure 9 shows additional peaks to those in Figure 8, which correspond to the tetragonal $PbTiO_3$ phase (labeled with the hkl's). The 3PG·PT and PG·3PT compositions show similar XDR patterns as shown in Figure 9 for the PG·PT composition, except that the ratios of the PG and PT phases change. The heat treatment variations investigated in processing the PG-PT compositions do not change the XRD patterns, indicating the existence of a two phase stability region of PG and PT. The results shown in Figures 8 and 9 also indicate that the $Pb_5Ge_3O_{11}$ and $PbTiO_3$ phases are fully crystallized by 600°C.

IV. SUMMARY AND CONCLUSIONS.

Glass compositions in the $Pb_5Ge_3O_{11}$-$PbTiO_3$ system were prepared by water and roller quenching methods. The low softening points in these glasses from 333 to 407°C indicate the potential of densification at very low temperatures. Exposure of these glasses in powder form to water induces crystallization of a metastable phase (see Reference 42), preventing densification from the softening of the glass. However, these compositions crystallize into a diphasic ferroelectric material by 600°C, and densify to 93-99% of the theoretical density at 700-720°C. This research demonstrates the possibility of designing a ferroelectric glass-ceramic system, which crystallizes completely into multiple ferroelectric phases and densifies at low temperatures, compared to previously developed ferroelectric glass-ceramic systems where nonferroelectric residual glass matrices remain.

ACKNOWLEDGMENTS

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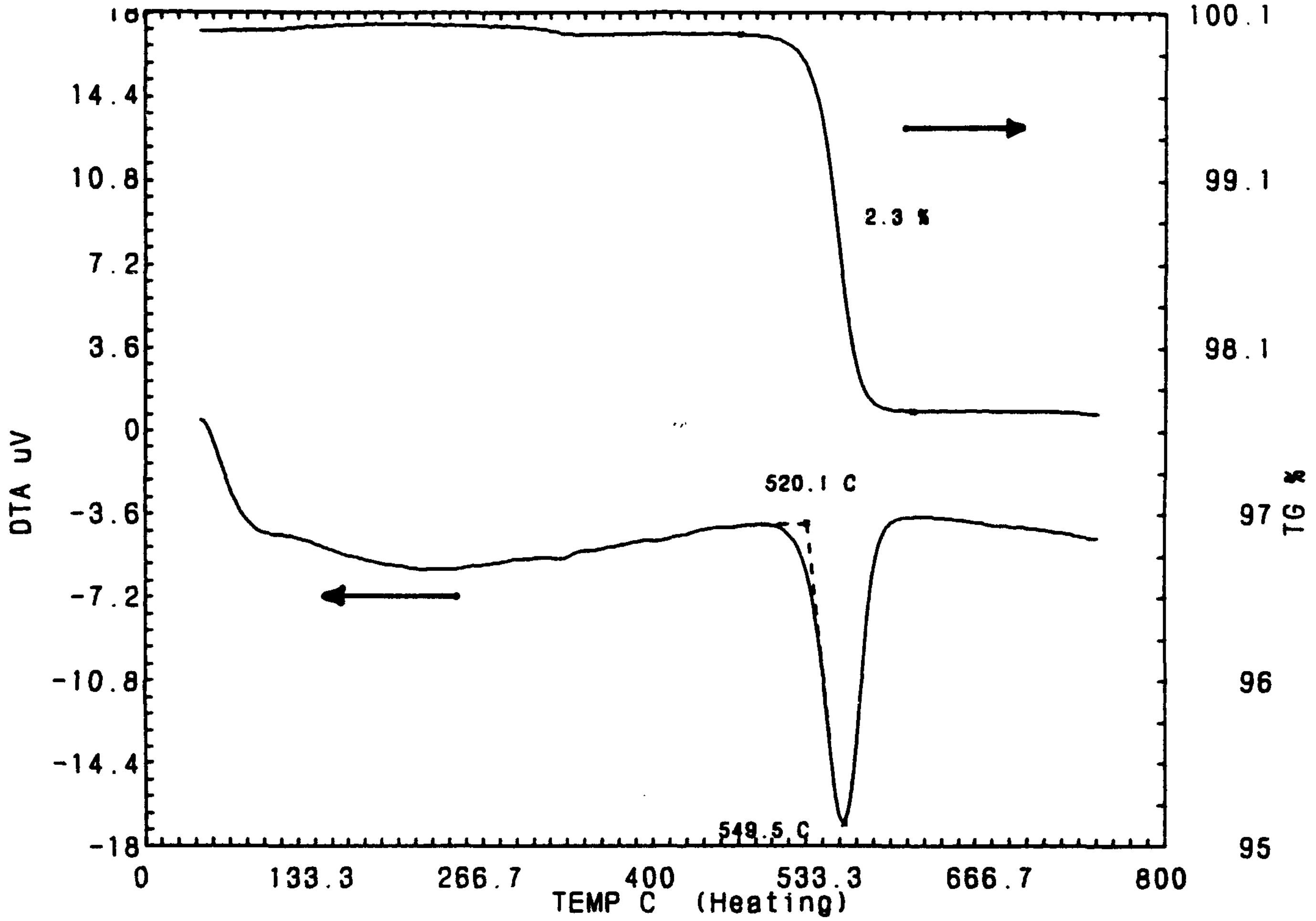

Figure 1. DTA (lower curve) and TGA (upper curve) profiles of Pb_3O_4 powders. The onset of the endothermic peak in the DTA curve at 520°C occurs because of the reduction of Pb_3O_4 to PbO, with the corresponding weight loss of 2.3% shown in the TGA curve.

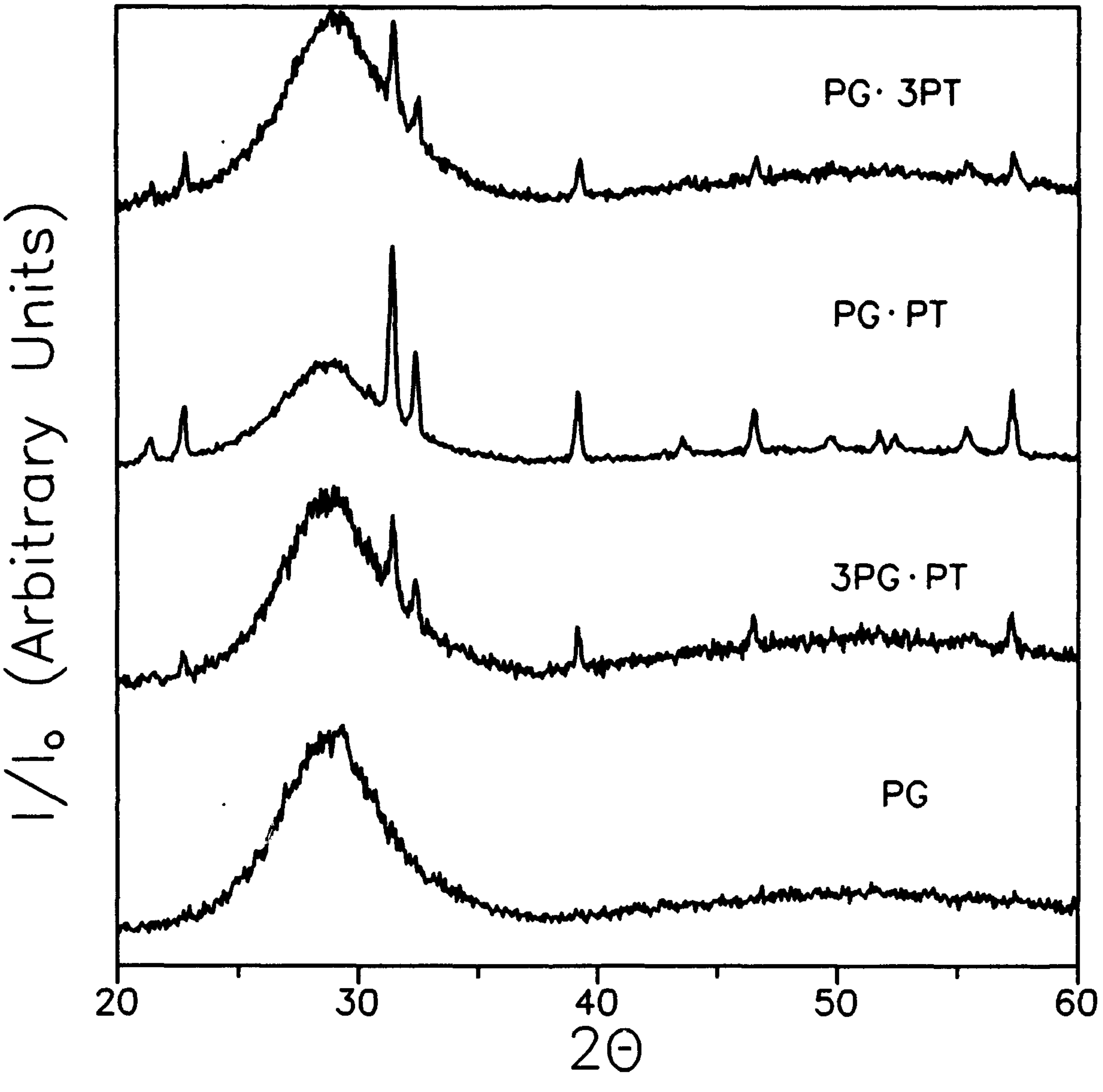

Figure 2. X-ray diffraction patterns of water quenched PG-PT glass powders which were prepared by dry grinding with a mortar and pestle.

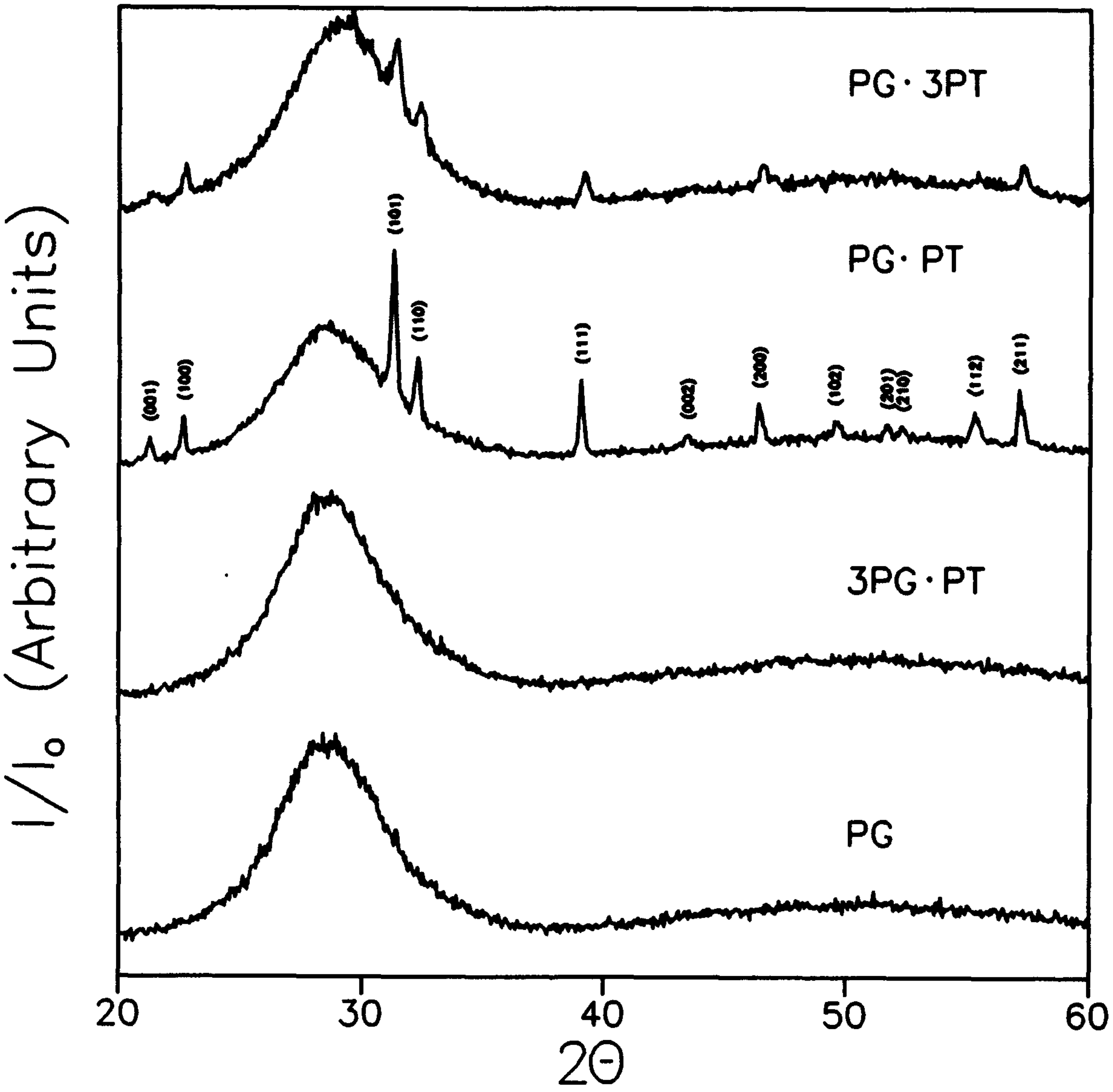

Figure 3. X-ray diffraction patterns of roller quenched PG-PT glass powders which were prepared by dry grinding with a mortar and pestle.

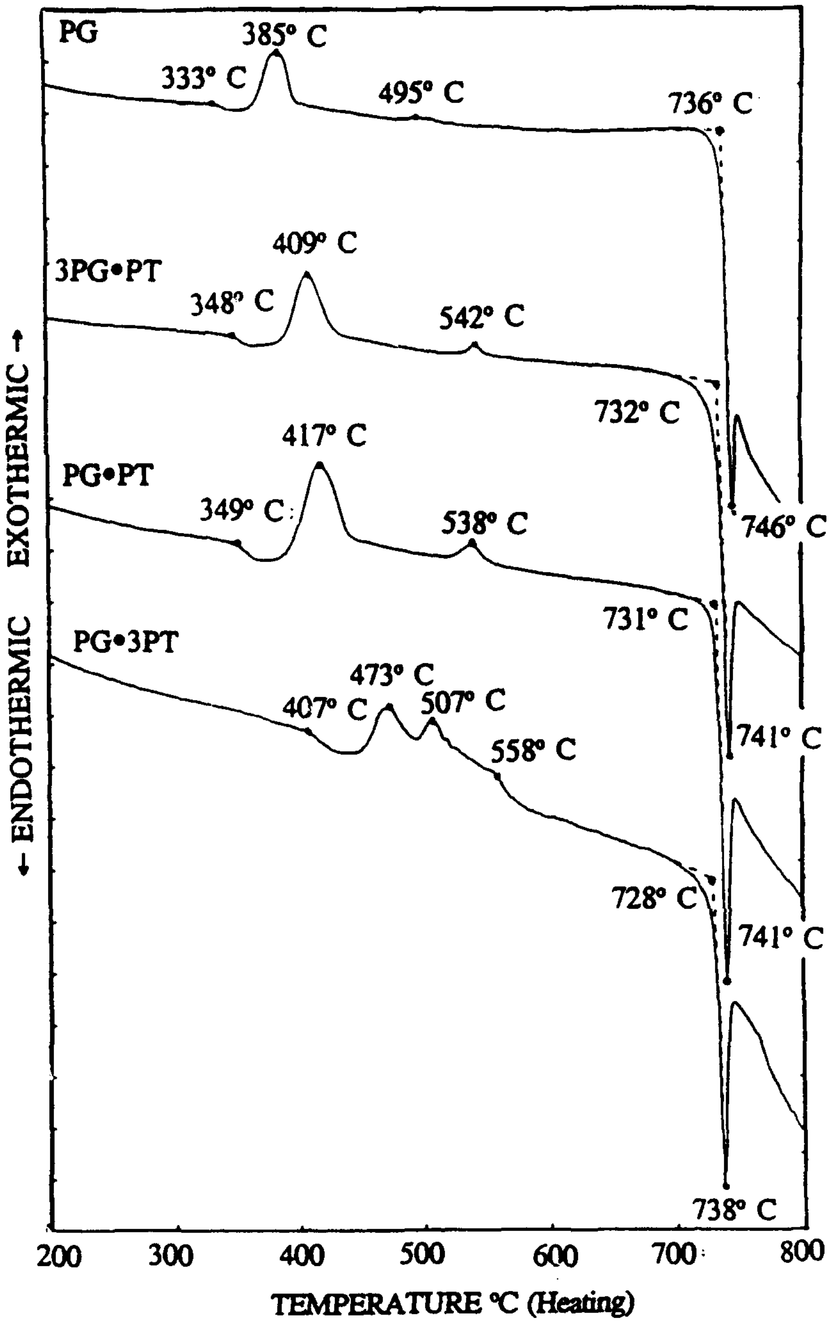

Figure 4. DTA patterns (on heating) of the same powders with XRD patterns shown in Figure 3.

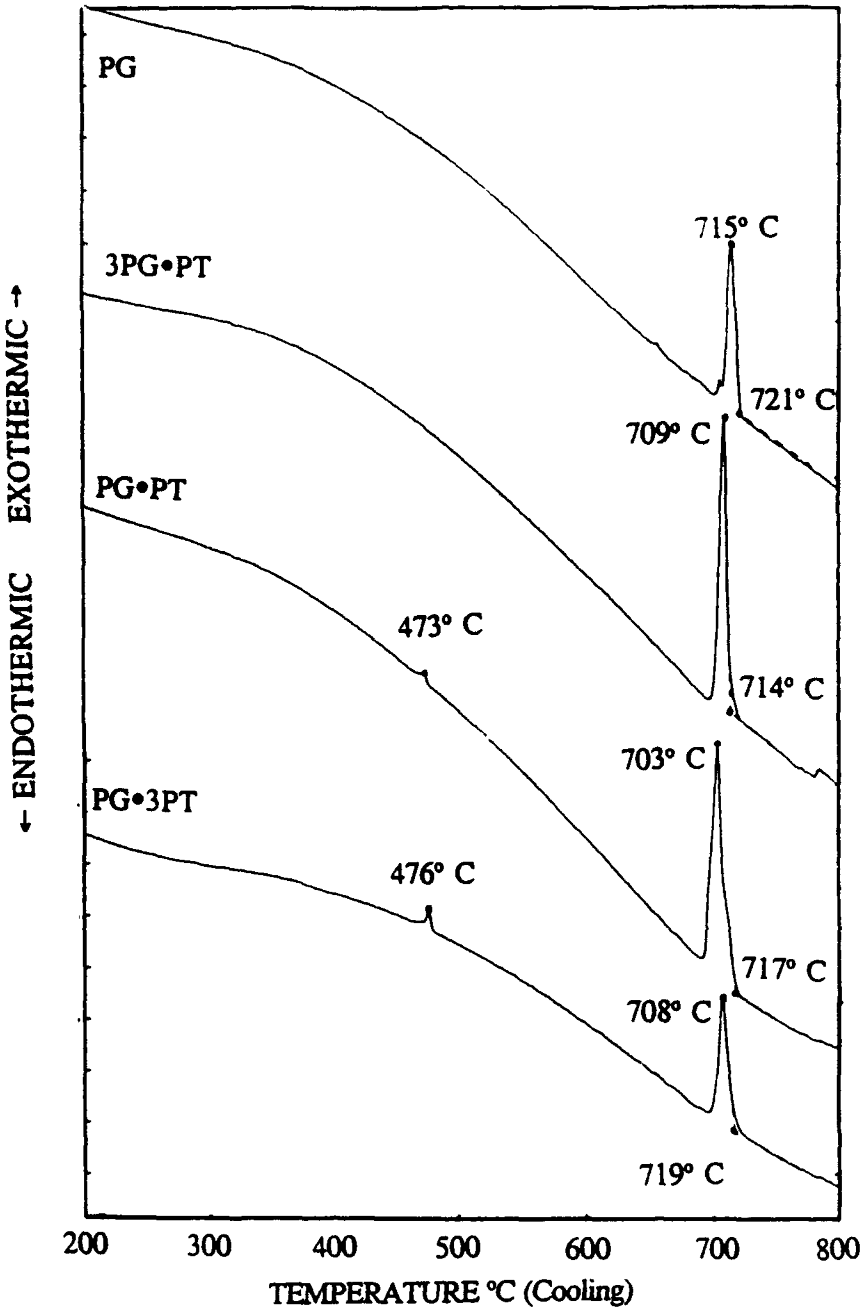

Figure 5. DTA patterns (on cooling) of the same powders with XRD patterns shown in Figure 3.

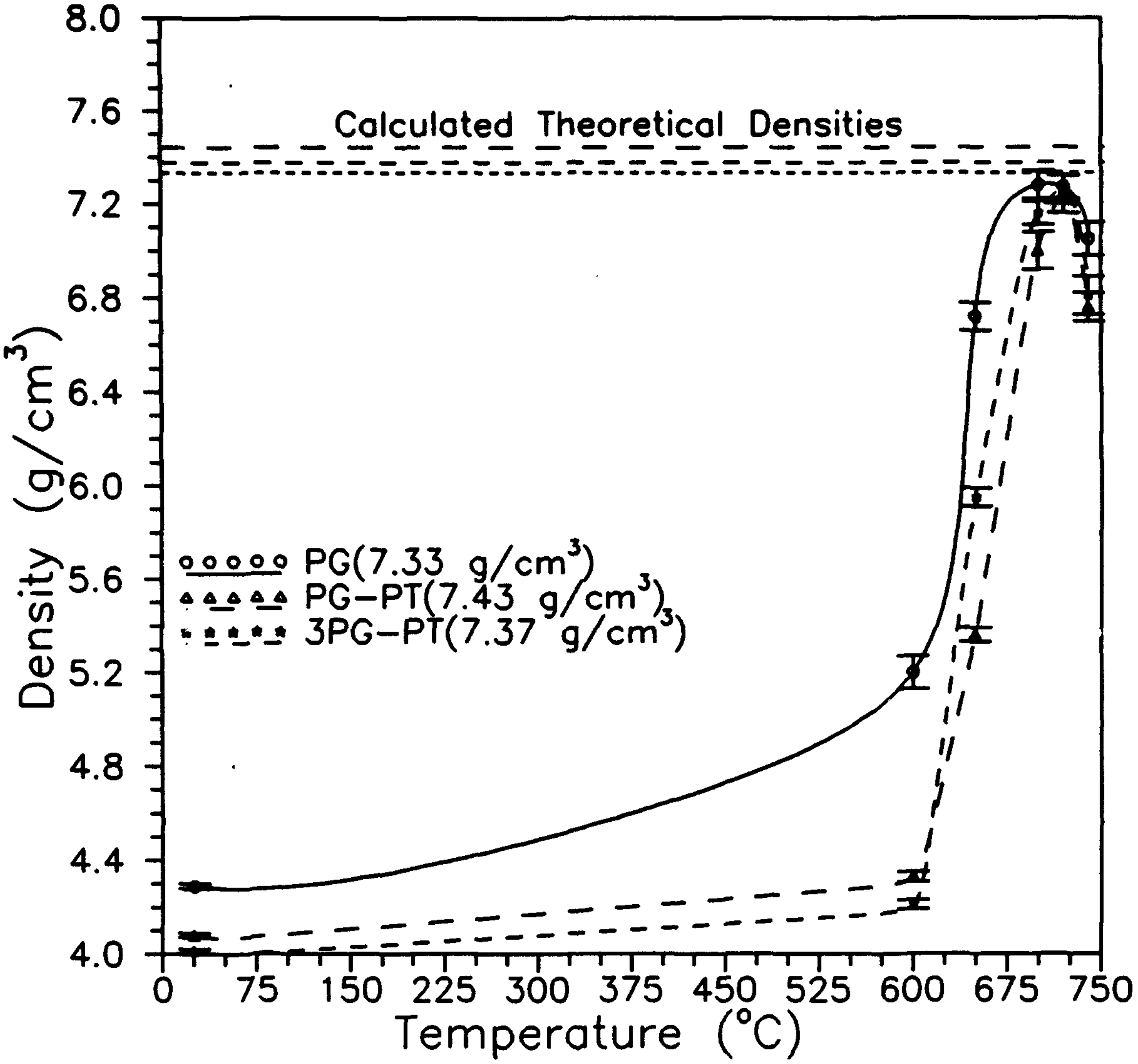

Figure 6. Density as a function of heat treatment temperature for pressed pellets of water ball milled glass powders. The upper two dashed curves are calculated theoretical densities (ρ_C), based on PG and PT theoretical densities of ρ_{PG}=7.33 and ρ_{PT}=7.966 g/cm^3, and using the following relation $\rho_C=\nu_{PG}\rho_{PG}+\nu_{PT}\rho_{PT}$, where ν is the volume fraction.

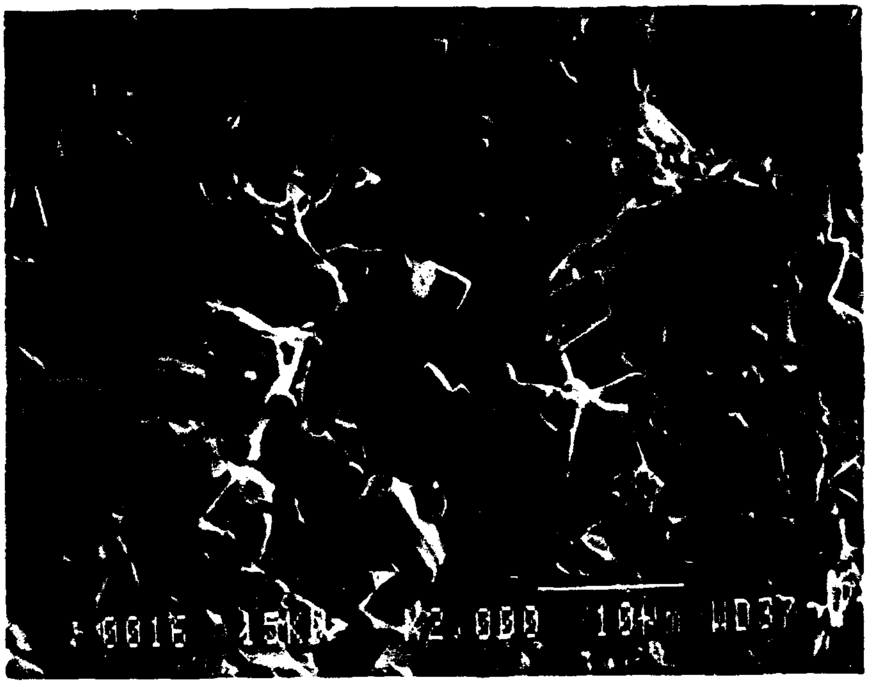

Figure 7. SEM micrograph of a fracture surface of a pellet of the PG·PT composition heat treated at 740°C for 2 hours.

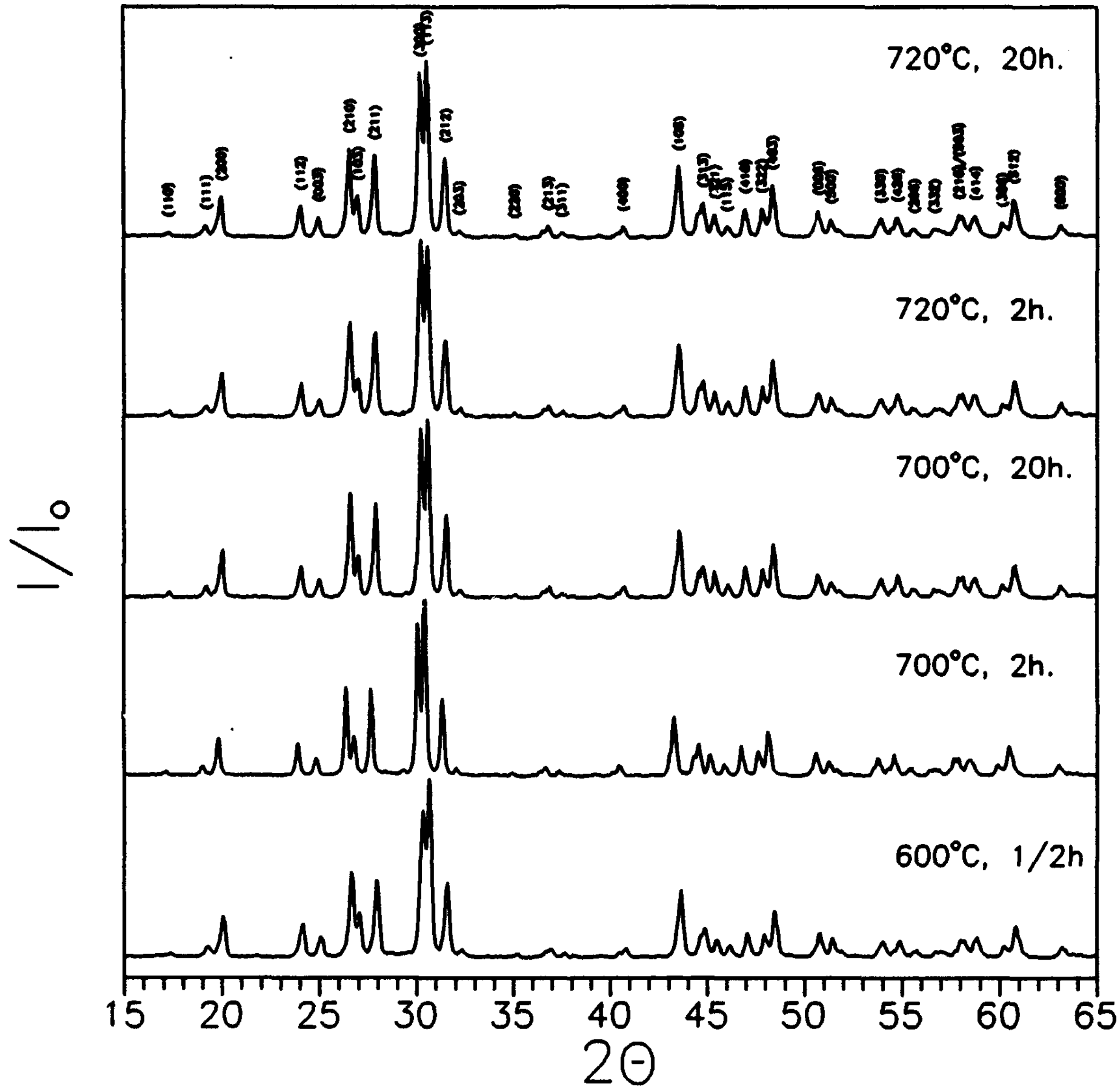

Figure 8. X-ray diffraction patterns of the pure PG composition heat treated at different temperatures and times.

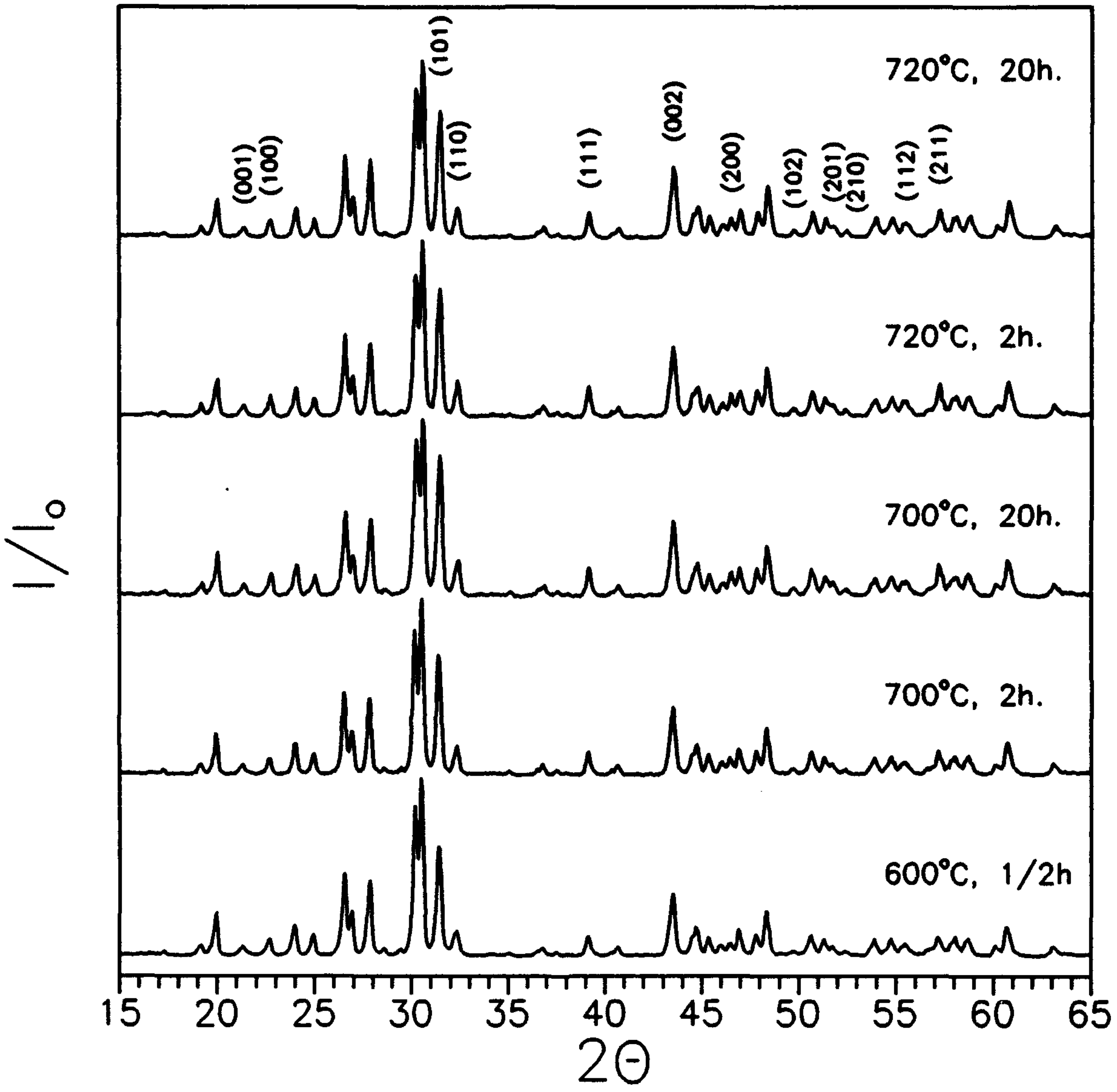

Figure 9. X-ray diffraction patterns of the PG·PT composition heat treated at different temperatures and times.

APPENDIX 8

Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part II: The $Pb_5Ge_3O_{11}$-$Pb(Zr_{1/2}Ti_{1/2})O_3$ System

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ABSTRACT

Melt derived amorphous compositions in the $Pb_5Ge_3O_{11}$-$Pb(Zr_{1/2}Ti_{1/2})O_3$ (PG-PZT) system were prepared by water and roller quenching methods. The crystallization behavior of this system was investigated by Differential Thermal Analysis (DTA), powder x-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The glass softening and crystallization temperatures were found to increase as the PG/PZT ratio decreases. A double melting point is observed by DTA measurements, indicating the presence of Pb_3GeO_5 along with the PG and PZT ferroelectric phases. The results obtained in the previously reported PG-PT system were directly applied to this system to crystallize and densify the PG-PZT compositions at low temperatures. This research appears to be the first to crystallize PZT from a melt-derived amorphous material.

I. INTRODUCTION.

The crystallization behavior of the glass-ceramic $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) system was reported in Part I of this paper [1]. This system crystallizes into a diphasic PG and PT ferroelectric material by 600°C, and densifies to 93-99% of the theoretical density between 700-720°C. These results suggest the potential of designing new ferroelectric glass-ceramic systems, which crystallize into multiple ferroelectric phases at low temperatures by combining the glass formability of PG with the excellent properties of a well known ferroelectric material.

A variety of approaches have been investigated to lower the processing temperatures of ferroelectric materials for capacitor and piezoelectric applications. These approaches have been reviewed previously [1-3], and will not be discussed in detail here. However, one of these approaches has involved additions of $Pb_5Ge_3O_{11}$ [4-7] or $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ [8-9] as a low melting crystalline phase to other crystalline ferroelectric phases. As discussed below there are significant differences in the processing methods used in the previous research compared to that presented in this paper.

Crystalline $Pb_5Ge_3O_{11}$ has been added to PLZT [4], PZT [5] and $Pb(Fe_{2/3}W_{1/3})O_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$ [7] to form a low melting liquid phase and reduce the sintering temperature. Schulze and Biggers [5] also demonstrate an additional benefit of stabilizing the PZT phase from depoling by incorporating an insulating grain boundary phase.

Payne et al. extended their earlier work of combining $Pb_5Ge_3O_{11}$

with $BaTiO_3$ [6] to also include additions of lead germanium silicate [8-9]. The starting PG and PGS compositions were prepared by melting, but the authors do not indicate whether the resulting powders were crystalline, amorphous, or a mixture of both [6,8-9].

In this research a new ferroelectric glass-ceramic system, $Pb_5Ge_3O_{11}$-$Pb(Zr_{1/2},Ti_{1/2})O_3$ was investigated. Here, the PG-PZT compositions studied are initially amorphous and by controlled heat treatments crystallize into multiple ferroelectric phases, densifying to closed porosity by 700°C. Apparently, in the literature there are not any references to melt-derived PZT glass-ceramics other than references 2, 10, 12, and 13. B. Houng and M.J. Haun [10] have investigated the glass-ceramic system of PZT in a lead borosilicate matrix. Glass ribbons of these compositions have been prepared by a roller quenching technique. Pressed glass powders heat treated at 850°C have piezoelectric d_{33} and g_{33} coefficients of 23 pC/N and $43 \cdot 10^{-3}$ Vm/N, respectively.

II. EXPERIMENTAL PROCEDURE.

Four different compositions, PG, 3PG·PZT, PG·PZT, and PG·3PZT were prepared from reagent grade Pb_3O_4, TiO_2, and ZrO_2 and electronic grade GeO_2. The sample preparation and characterization procedures used are similar to that described for the glass-ceramic PG-PT system in Part I of this paper [1].

III. RESULT AND DISCUSSION.

XRD patterns of the roller quenched PG-PZT glasses ground in a mortar and pestle are shown in Figure 1. The $Pb_5Ge_3O_{11}$ and $3Pb_5Ge_3O_{11} \cdot Pb(Zr_{1/2}Ti_{1/2})O_3$ compositions are completely x-ray amorphous. The other two compositions with further additions of PZT are mostly amorphous, but have small crystalline peaks. In the PG·PZT composition all of the observed peaks correspond to the desired PZT phase, and the broadness of these peaks indicate small grain size (submicron range) of the PZT crystallites. In the PG·3PZT composition (top curve in Figure 1) XRD peaks from the ferroelastic and possibly antiferroelectric Pb_3GeO_5 phase [11] is observed in addition to the peaks from the PZT phase. A broad unidentified peak centered at ≈42 degrees two theta was also observed.

Differential Thermal Analysis (DTA) has been measured at 10°C/min in a flowing nitrogen atmosphere for both the water quenched [12] and roller quenched [13] glass powders which were prepared by dry grinding with a mortar and pestle. The results obtained were very similar in both cases. Figure 2 shows the DTA patterns of the roller quenched glass powders of the PG-PZT system upon heating. Endothermic shifts occur in the baseline corresponding to the softening and densification of the glass powders at temperatures from 333 to 373°C. The first exothermic crystallization peaks occur at temperatures from 385 to 430°C. The separation of the softening and crystallization temperature ranges indicates the potential of densification at very low temperatures (≤373°C). These softening and densification temperatures are lower in this system compared to the PG-PT system [1].

Figure 2 also shows that endothermic peaks occur at higher temperatures around 700-740°C. Addition of PZT to the pure PG composition creates a double "melting" point at an onset temperature of ≈703°C in coexistence with that at ≈730°C. The endothermic peak at ≈703°C increases as the PG/PZT ratio decreases. In the PG·3PZT composition only the lower temperature endothermic peak is present. These results corroborate those shown in Figure 1, and also indicate the coexistence of the $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 phases together with the PZT phase. The onset of the first endothermic peak at 703°C corresponds to the eutectic point between the 5:3 and 3:1 phases in the $PbO-GeO_2$ phase diagram reported by Hasegawa et al. [14].

The presence of the nonferroelectric Pb_3GeO_5 phase in the PG-PZT system has been reported by Schulze and Biggers [5]. They suggest that the $Pb_5Ge_3O_{11}$ phase takes PbO from the PZT phase to form the observed Pb_3GeO_5 phase. However, in our experiments we have observed that higher melting temperatures are needed when the ZrO_2 content increases, and possibly some zirconia is left in the crucible when the molten liquid is poured. In this case, the resulting glass will be rich in lead, promoting the formation of the Pb_3GeO_5 phase. Further research is needed to confirm this.

On cooling the PG-PZT system, the DTA exhibits two large exothermic peaks from recrystallization of the ferroelectric PG and non-ferroelectric Pb_3GeO_5 phase (Figure 3). These crystallization peaks and the "melting" peak in Figure 2 show a hysteretic behavior similar to the PG-PT system [1], indicating the presence of superheating and supercooling. However, the temperature of the solidus line in the PG-PZT system can not be conclusively determined, because of the presence of the Pb_3GeO_5 phase.

In Figure 3 no other exothermic peaks occur at lower temperatures as was observed in the PG-PT system. This is because $Pb_5Ge_3O_{11}$ and $Pb(Zr_{1/2}Ti_{1/2})O_3$ exhibits a second order transition from a paraelectric to a ferroelectric phase at 177 and 390°C, respectively [15-16]. With second order phase transitions a latent heat and resulting exothermic DTA peak do not occur.

PG-PZT glass powders that come in contact with water were found to induce crystallization of the same unknown metastable phase (or phases) reported in the PG-PT system [1]. The crystallization of this phase (or phases) is more extensively discussed in Reference 17.

Based on the results obtained from the PG-PT system [1], the PG-PZT compositions were heat treated with selected conditions as is indicated in Figure 4. The XRD patterns in Figure 4 show that in addition to the peaks from the ferroelectric phases $Pb_5Ge_3O_{11}$ and $Pb(Zr,Ti)O_3$, the nonferroelectric Pb_3GeO_5 phase also coexists in minor proportions as expected from the DTA results. An unidentified phase is also present which appears to increase in amount as the processing temperature increases.

With further optimization of the processing, such as completely dissolving the ZrO_2, these minor undesired phases can probably be eliminated. Even with these phases the room temperature dielectric constant doubles in the PG-PZT compositions as compared with that of the pure PG [12]. The ferroelectric hysteresis loop of a thick film sample of the same composition shows a maximum polarization of 7.2 $\mu C/cm^2$, further indicating the influence of the PZT phase [2].

Assuming that the only phases present are PG and PZT, the PG·PZT composites should have a calculated theoretical density of 7.45 g/cm^3. The measured densities (using the Archimedes' method) of the samples with XRD patterns shown in Figure 4 range from 6.81-7.37 g/cm^3. The sample heat treated at 700 and 740°C (top curve in Figure 4) had the lowest density, while heat treating at 740 and then at 700°C resulted in the highest density (middle curve in Figure 4). The SEM micrograph of the fractured surface of these samples show the hexagonal platelet structure of $Pb_5Ge_3O_{11}$ phase (see Figure 5).

IV. SUMMARY AND CONCLUSIONS.

Glass compositions in the $Pb_5Ge_3O_{11}$-$Pb(Zr,Ti)O_3$ system were prepared by water and roller quenching methods. These compositions crystallized into multiple ferroelectric phases (PG and PZT) at low temperatures ($\leq$700°C). A minor amount of the nonferroelectric Pb_3GeO_5 phase also crystallized indicating that the composition may be slightly off stoichiometry, possible because of partially undissolved ZrO_2 during melting. A two step heat treatment (740°C for 5 hours, followed by 700°C for 5 hours) was found to densify these compositions to closed porosity. This research appears to be the first to crystallize PZT from a melt-derived amorphous material.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (contract # DMR-9158312) and the Office of Naval Research (contract # N00014-92-5-1390)

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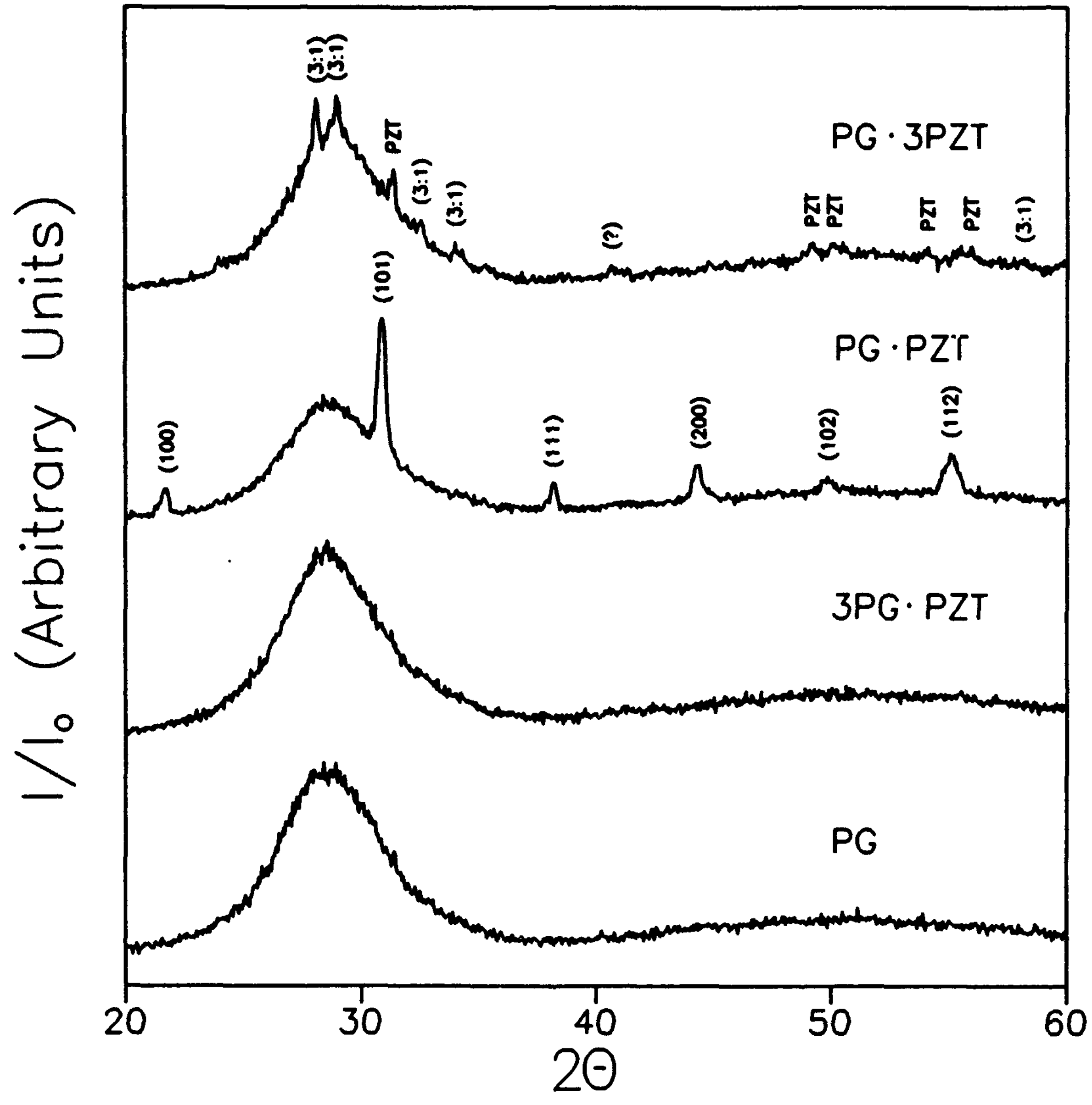

Figure 1. X-ray diffraction patterns of water quenched PG-PZT glass powders which were prepared by dry grinding with a mortar and pestle. All of the (hkl) peaks labeled in composition PG·PZT correspond to the PZT phase. In composition PG·3PZT, in addition to the PZT phase the nonferroelctric Pb_3GeO_5 is also observed.

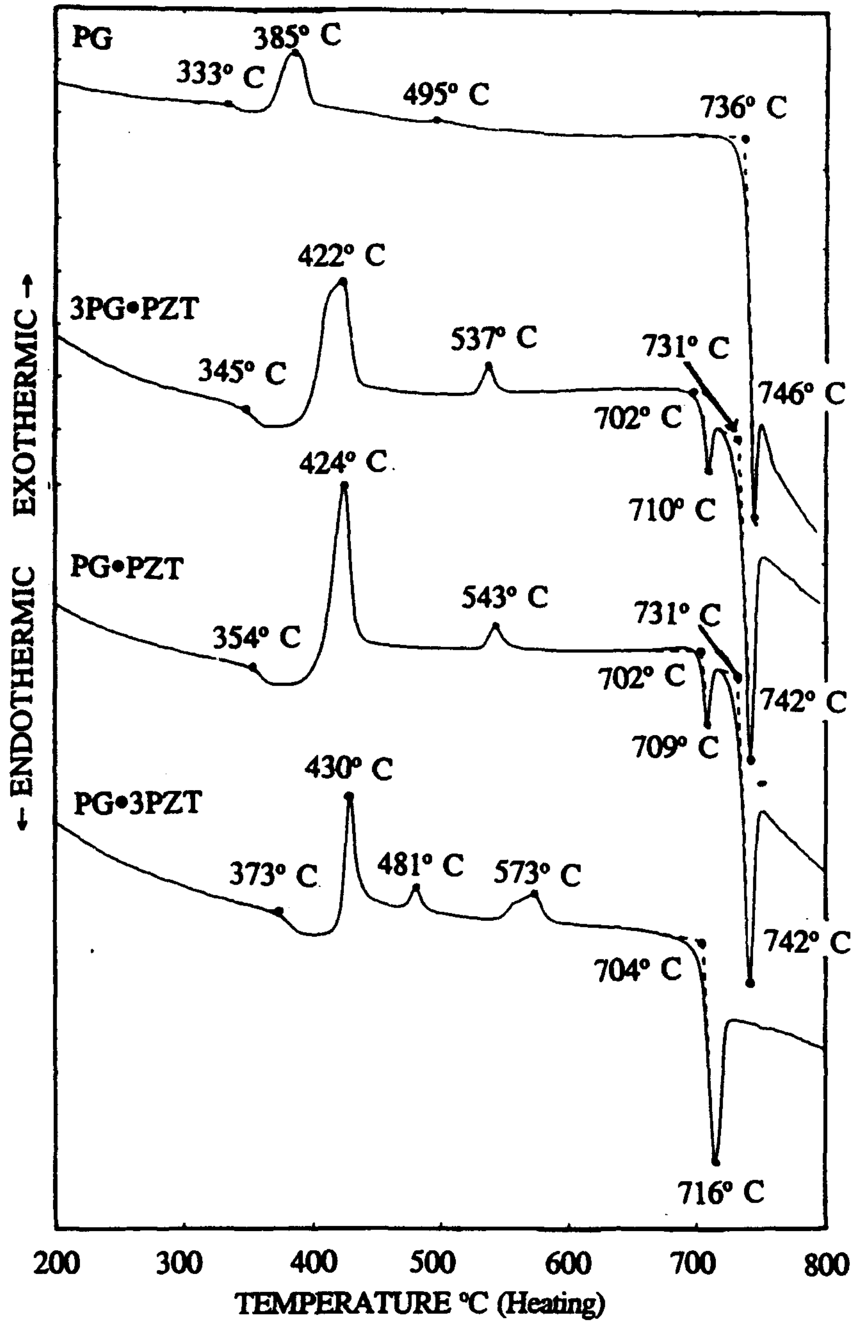

Figure 2. DTA patterns (on heating) of the same powders with XRD patterns shown in Figure 1.

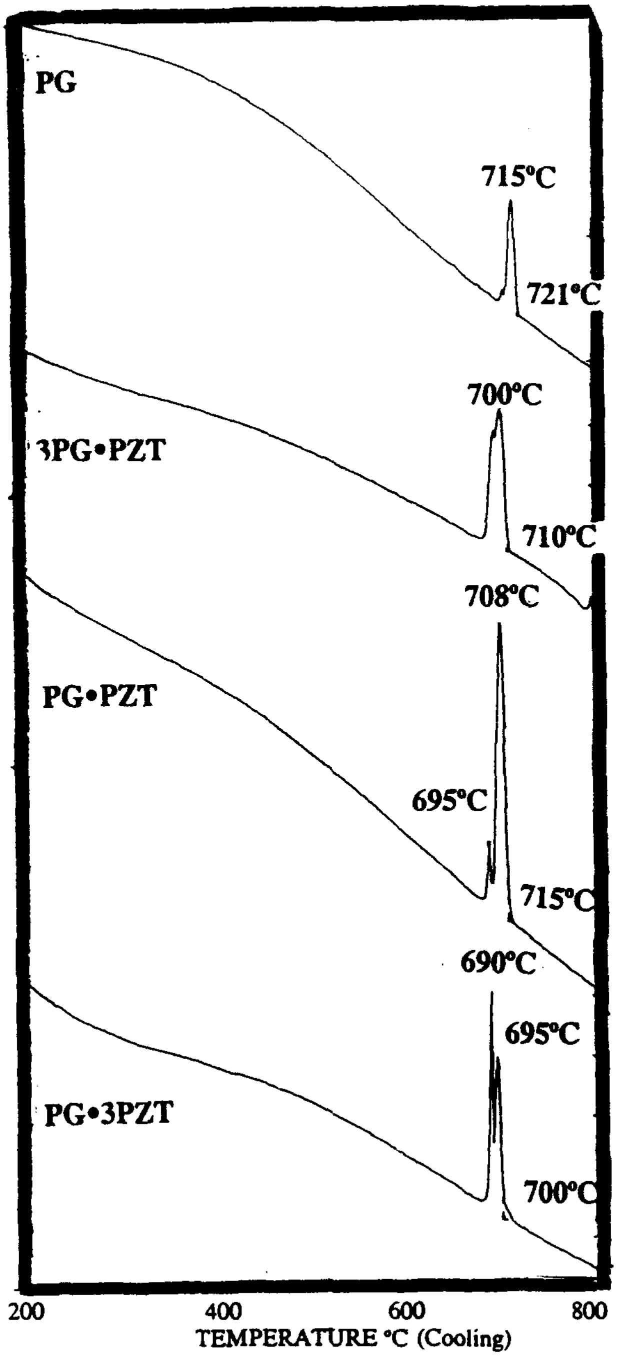

Figure 3. DTA patterns (on cooling) of the same powders with XRD patterns shown in Figure 1.

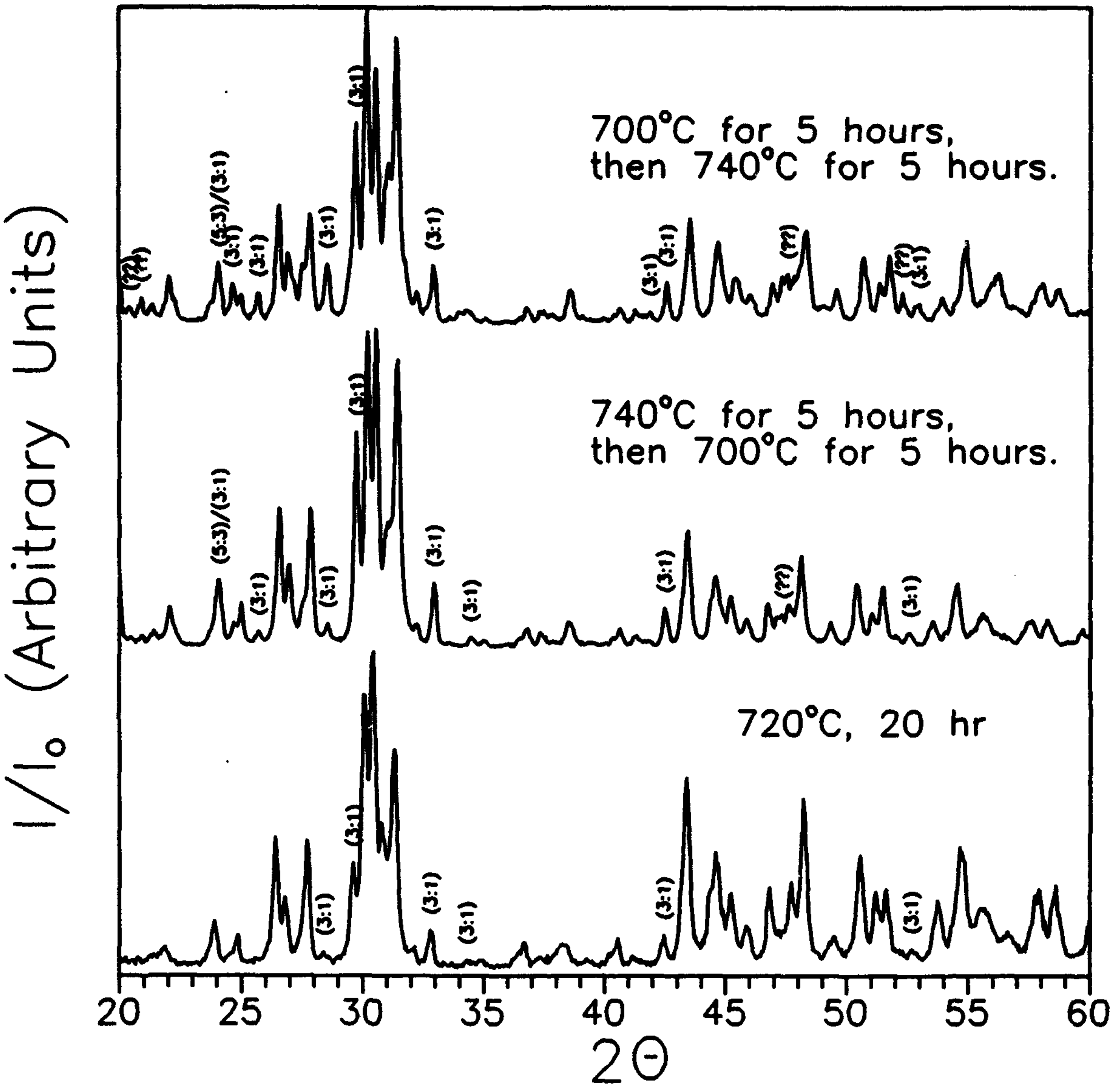

Figure 4. X-ray diffraction patterns of the PG·PZT composition heat treated at different temperatures and times. All of the unlabeled peaks correspond to ferroelectric PG or PZT phases. The nonferroelectric Pb_3GeO_5 (3:1) and an unknown (??) phases are indicated.

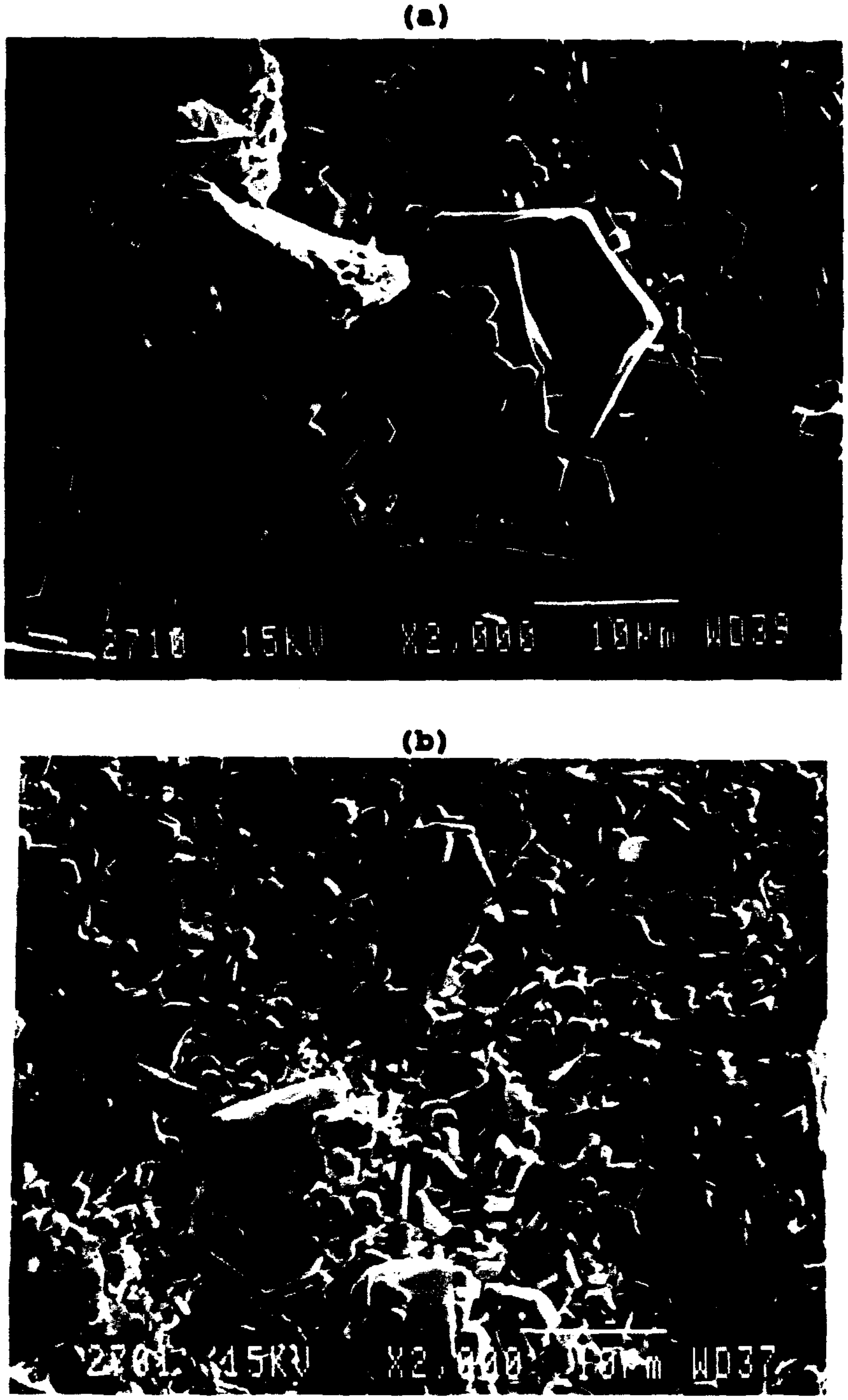

Figure 5. SEM micrographs of fracture surfaces of pellets of the PG·PZT composition heat treated at: (a) 700°C for 5 hours, then 740°C for 5 hours, and (b) 740°C for 5 hours, then 700°C for 5 hours.

APPENDIX 9

Water Induced Crystallization of a Metastable Phase from Melt Derived $Pb_5Ge_3O_{11}$ Based Amorphous Compositions

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ABSTRACT

The densification behavior of glass powder compacts of $Pb_5Ge_3O_{11}$ (PG), $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ (PGS), $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT), and $Pb_5Ge_3O_{11}$-$Pb(Zr,Ti)O_3$ (PG-PZT) is affected by the processing conditions. In particular, if a liquid medium is used in the ball milling process the densification and crystallization behavior can be significantly affected. The results obtained in this investigation show that methanol and acetone mediums do not affect the amorphous degree of the glasses, however, these liquids adversely affect the final density even after heat treatments at 720°C for 20 hours. All of the PG-based glass powders in contact with water develop an unknown metastable crystalline phase at room temperature. The crystallization of this phase does not allow densification to occur from the softening of the glass at low temperatures. However, pressed pellets of these water ball milled glass powders densify to 93-99% of the theoretical density at 620°C for the PGS glass, and at 700°C for the PG, PG-PT, and PG-PZT glasses. In addition, the metastable phase transforms to the desired ferroelectric phases by 600°C.

I. INTRODUCTION.

Ferroelectricity in $Pb_5Ge_3O_{11}$ (PG) was independently discovered by Iwasaki et al.[1], and by Nanamatsu et al.[2] in 1971 in single crystals prepared by the Czochralski and Bridgman methods, respectively. The isomorphous ferroelectric compound $Pb_5Ge_2SiO_{11}$ (PGS) was first reported by Iwasaki et al. in 1972 [3] in a single crystal grown by the Czochralski method. In 1973 Eysel et al. [4] found that a solid solution of $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ with up to 62% Si replaced for Ge can be formed. Furthermore, PG and PGS were found to form glass relatively easily, and crystallize into a ferroelectric phase [4-7].

Lead germanate-based glasses and glass-ceramic systems have been investigated recently [8-13]. $Pb_5Ge_3O_{11}$ was combined with $PbTiO_3$ (PT) and $Pb(Zr_xTi_{1-x})O_3$ (PZT) to form unique ferroelectric glass ceramic systems which crystallize into multiple ferroelectric phases at 600°C. All of these glasses possess low softening temperatures, suggesting the potential of densification at temperatures below 410°C. However, the liquid used for processing the PG-based glass compositions limits the densification at these low temperatures. Higher temperatures close to the melting point of PG have been generally necessary to achieve closed porosity samples.

The parameters involved in growing defect free PG single crystals are well known [14]. However, previous research to densify PG and PGS pressed powders has resulted in a wide range of densification behavior and homogeneity without a clear understanding of the critical parameters involved. Eysel et al. [4] found that solid state reactions to form PGS solid solutions were sluggish, and yielded poorly crystallized ceramic. Thus, to improve the formation of homogeneous and dense compositions, they melted and re-crystallized PGS. Jones et al. [15] prepared PG ceramic pellets at 700°C for 12 hours, which resulted in good ceramic samples with 15-20 μm particle size and $\approx$1 volume percent porosity, however no specifications about batch preparation was mentioned. Luff et al. [16] did a series of studies on ferroelectric ceramics with high pyroelectric activity, among them the PG compound. They found that sintering was very critical, and 100% of the theoretical density was reached in samples fired at 700-720°C. In addition, only samples wet ball milled in large water/powder ratios reached the zero porosity reported. Dry ball milled powders sintered in pellet form were inhomogeneous and contained pin-holes.

In this paper, an investigation of various processing conditions on the densification behavior of PG, PGS, PG-PT, and PG-PZT glass powders is presented. The effect of the liquid used for wet ball milling is related to the densification problems previously encountered by other investigators in sintering PG and PGS ceramics.

II. EXPERIMENTAL PROCEDURE.

The compounds $Pb_5Ge_3O_{11}$ (PG) and $Pb_5Ge_2SiO_{11}$ (PGS), and compositions from the $Pb_5Ge_3O_{11}$-$PbTiO_3$ (PG-PT) and $Pb_5Ge_3O_{11}$-

$Pb(Zr_{1/2},Ti_{1/2})O_3$ (PG-PZT) systems were prepared from reagent grade Pb_3O_4, TiO_2, ZrO_2, and SiO_2, and electronic grade GeO_2.

The batches were mixed either dry or in distilled water for five hours. The wet mixed powders were dried at 100°C for 20-24 hours before melting. The dry mixed powders were transferred to a platinum crucible directly after mixing for melting. The crucible was covered with a Pt-lid and placed into the furnace at temperatures from 800 to 1275°C, depending on composition, with a hold time of 15-20 minutes. A 70 weight percent Pb_3O_4 and 30 weight percent ZrO_2 unreacted mixture was utilized to control the lead volatility of the compositions which were melted above 900°C. The molten liquid was poured either into distilled water at ≈2°C or into a twin-roller quenching apparatus to produce glass ribbon. The glasses were then ball milled with ZrO_2 grinding media in either a liquid medium (distilled water, methanol, or acetone) or dry for twenty hours. The glass ribbon was also ground dry or wet (using distilled water, acetone, or methanol) in a mortar and pestle for three minutes. These wet ground powders were left in the same liquid medium in a closed container for 1 and 20 hours. Some of the dry ground ribbons were soaked in water at different temperatures and times. DTA and XRD were conducted on the powders before and after the ball milling and the grinding processes. After ball milling, the slurry was screened through a 45 μm (325 mesh) sieve, and dried at 100°C. The dry milled powders were screened through a 75 μm (200 mesh) sieve. The dry mortar and pestle ground powders of PG ribbon were also screened through a 45 μm sieve. Pellets 13 mm in diameter and 1-2 mm thick were pressed without binder at a pressure of 10 ksi for one minute. After heat treatment at 700°C for 2 hours, the samples were analyzed with XRD and SEM, and densities measured geometrically.

III. RESULTS AND DISCUSSION.

Water ball milled glasses of all of the compositions studied crystallized an unidentified metastable phase that does not appear to match any of the JCPDS x-ray diffraction cards. Figures 1 and 2 show x-ray diffraction patterns of water-quenched glasses before and after 20 hours of water ball milling. A small amount of crystallization of the desired ferroelectric phases is observed in Figure 1, which occurs depending on the quenching conditions and the time needed to transfer the crucible from the furnace to the quenching set up [12-13]. The dramatic increase in crystallization in Figure 2 is independent of composition and quenching conditions. The phase (or phases) formed is metastable and transforms to the stable ferroelectric phases by 600°C. This phase occurs in powders that come in contact with water at room temperature.

The crystallization of this metastable phase is not related to the ball milling process, as is demonstrated in Figure 3, where XRD patterns of roller quenched PG glass ground in different liquids are shown. The amorphous character of PG remains when the powders are ground dry, or in methanol or acetone. However, powders that come in contact with water form the crystalline metastable phase (or phases) as shown in Figures 2 and 3. Because of this crystallization, the softening of the glass is lost and higher temperatures are then necessary to densify the samples. The results shown in Figure 3 suggest that a possible simple solution to this problem is to ball mill in acetone, methanol or dry. However, these powders were used to press pellets without binder at 10 ksi for 1-3 minutes. These pellets plus a 24-hour water ball milled sample were heat treated at 700°C for 2 hours. The resulting densities were measured geometrically.

Table 1 summarizes the effect of grinding method and liquid used on the structure and percent of the theoretical density of the PG composition. The mortar and pestle ground samples in acetone, methanol, and dry have an average density around 74%. However, those ground in the presence of water have a measured density of 81%, and the water ball milled of 97%. A comparison between the mortar and pestle dry ground powders reveals that screening through a 325 mesh sieve has no significant effect on the final density. However, the powders in contact with water have the highest densities, with the density of the water ball milled sample much higher than that of the water mortar and pestle ground sample.

These results appear to demonstrate that the particle size distribution of the powders in contact with water also affects the density. However, additional research is needed to further understand the effect of particle size on densification. These studies strongly suggest that the water induced metastable phase found in this research plays a key role in the densification mechanisms of PG based glass powders.

IV. SUMMARY AND CONCLUSIONS.

Densification problems in the PG, PGS, PG-PT, and PG-PZT ferroelectric glass-ceramic systems were investigated. Powders that come in contact with water induce an unknown metastable crystalline phase. This phase transforms to the stable ferroelectric phases by 600°C, but limits the densification of these glass compositions at the softening temperatures. However, only these powders densified to closed porosity at 700°C. On the other hand, glasses ball milled in acetone, methanol, or dry remain x-ray amorphous, but pressed powders do not densify well, even at high temperatures. Particle size and particle size distribution effects may play a key role in the densification behavior, and thus future research is needed to investigate these parameters.

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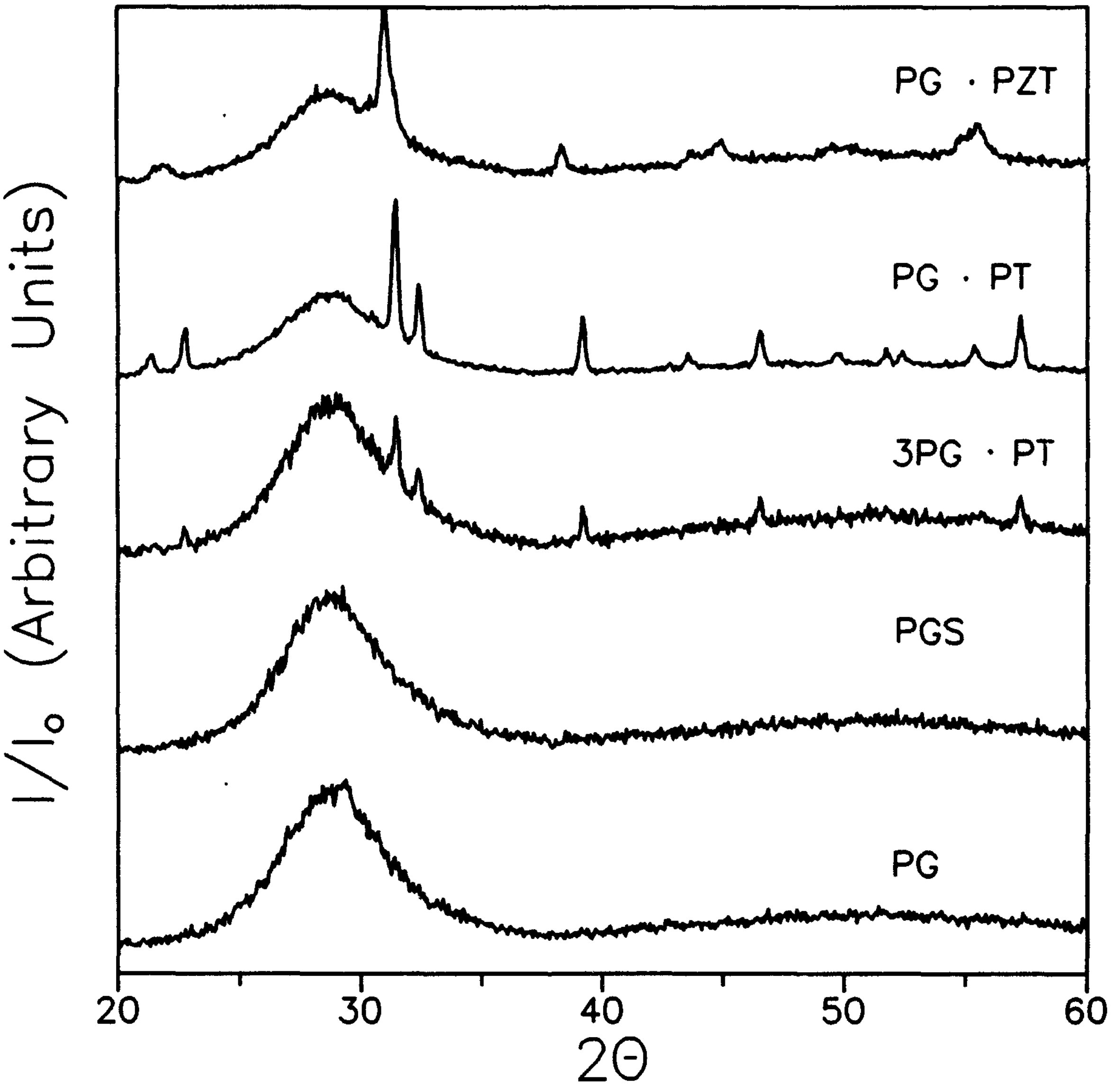

Figure 1. XRD patterns of different glass compositions quenched in water at 2°C and dry ground in a mortar and pestle. The observed crystalline peaks on the top three curves belong to the ferroelectric $PbTiO_3$ or $Pb(Zr_{1/2}Ti_{1/2})O_3$ phases. Compositions PG and PGS are x-ray amorphous.

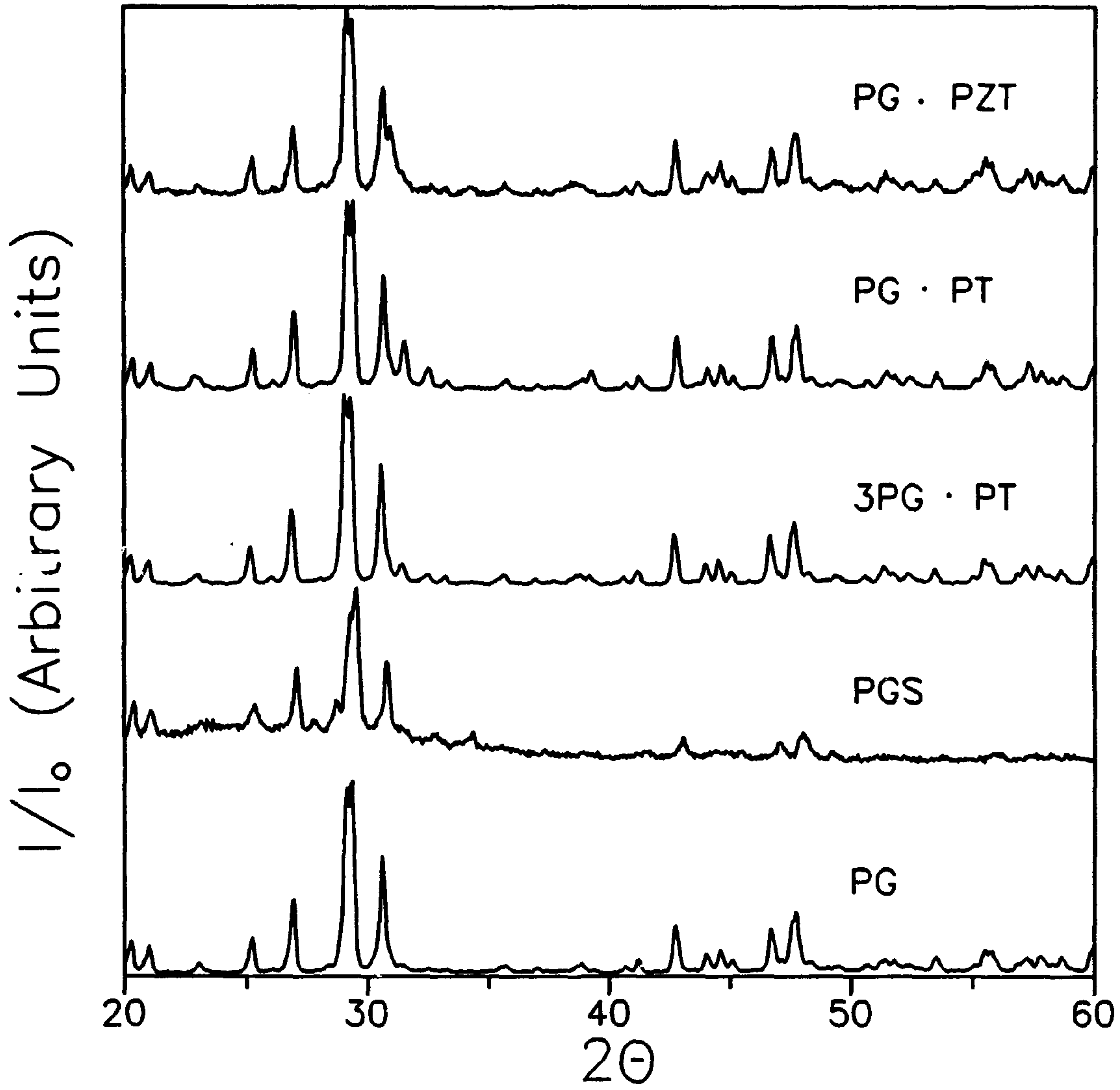

Figure 2. XRD patterns of the same compositions in Figure 1, after ball mill in water for 24 hours. All patterns show a crystalline water-induced metastable phase. The PGS composition appears to be less affected than the other compositions.

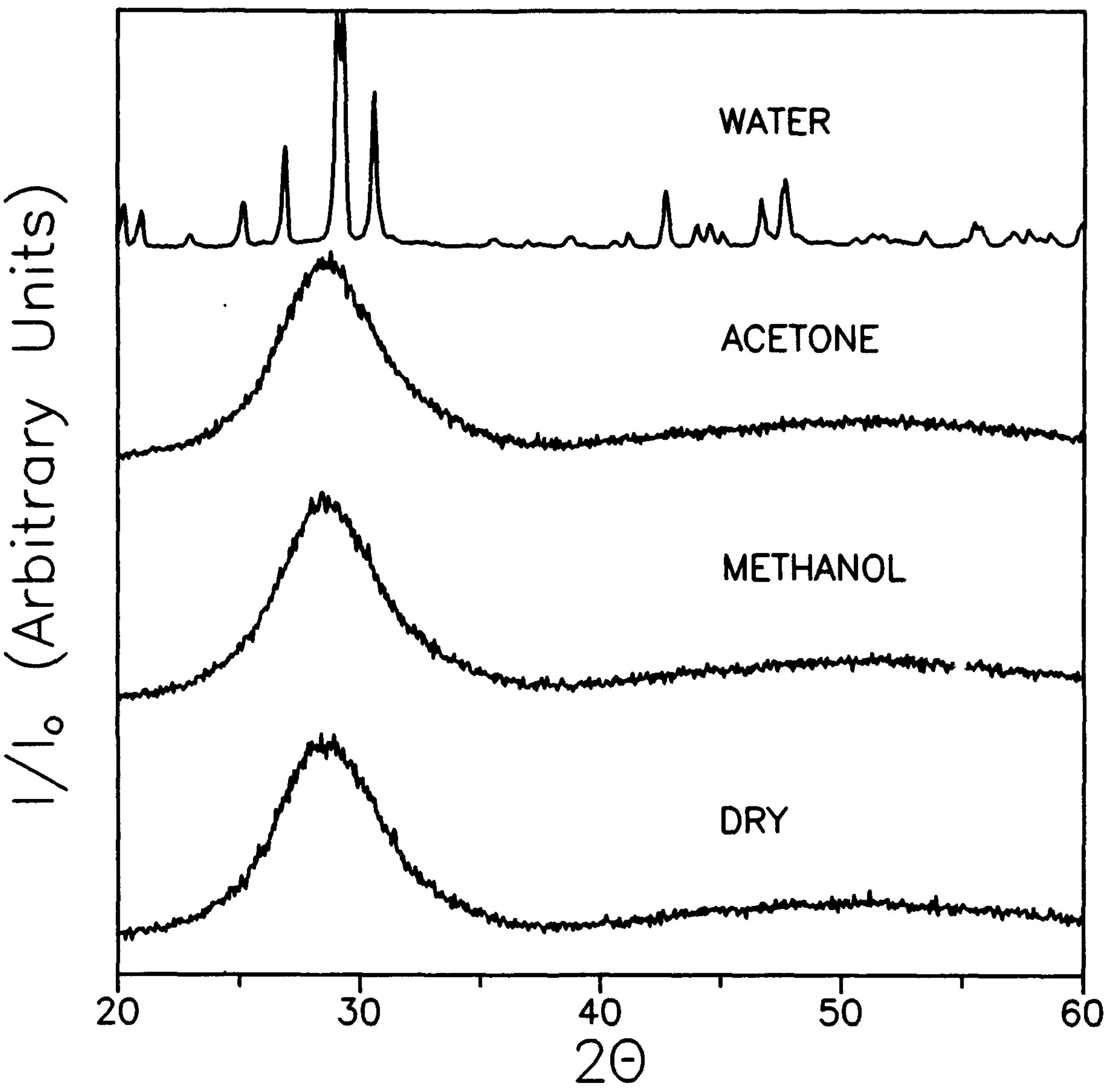

Figure 3. X-ray diffraction patterns of roller quenched PG glass compositions dry and wet ground in 'ifferent mediums with a mortar and pestle for 3 minutes and soaked in the same medium for 20 hours. Only those powders in contact with water develop the metastable phase, while the other compositions remain amorphous.

Table 1. Comparison of Grinding Method and Liquid Used on the Structure and Final Density of the PG Composition.

Grinding Method	Liquid Used (sieve size)	XRD Pattern	% of Theoretical Density
ball mill	water (325)	metastable	97*
ball mill	methanol (325)	amorphous	not evaluated
ball mill	none (200)	amorphous	not evaluated
mortar&pestle	acetone (none)	amorphous	73
mortar&pestle	methanol (none)	amorphous	76
mortar&pestle	none (none)	amorphous	74
mortar&pestle	water (none)	metastable	81
mortar&pestle	none (325)	amorphous	72

* Density Measured by the Archimedes' Method