

- Chem.* **1971**, 27, 241.
9. Kim, T. J.; Lee, K. C. *Bull. Korean Chem. Soc.* **1989**, 10, 279.
 10. Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorganic Synthesis* **1970**, 12, 238.
 11. Perin, D. D.; Armarego, W. L. F.; Perin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
 12. Benito, A.; Cano, J.; Martinez-Manez, R.; Soto, J.; Paya, J.; Lioret, F.; Julve, M.; Faus, J.; Marcos, M. D. *Inorg. Chem.* **1993**, 32, 1197.
 13. (a) Takegami, Y.; Watanabe, Y.; Kanaya, I.; Mitsudo, T.; Okajima, T.; Morishima, Y.; Masada, H. *Bull. Chem. Soc. Jpn.* **1968**, 41, 1990. (b) Shim, S. C.; Doh, C. H.; Kim, T. J.; Lee, H. K.; Kim, K. D. *J. Heterocyclic Chem.* **1988**, 25, 1383.
 14. Detailed crystallographic descriptions for **3a** appeared in the literature during the preparation of this manuscript. See: Tendro, M. J. L.; Benito, A.; Manez, R. M.; Soto, J.; Paya, J.; Edwards, A. J.; and Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1996**, 343.
 15. Sheldrick, G. M. SHELXS-86. Program for the solution of crystal structure determination. Univ. of Gottingen, Germany, 1985.
 16. Sheldrick, G. M. SHELXS-93. Program for the solution of crystal structure determination. Univ. of Gottingen, Germany, 1993.
 17. (a) Bracci, M.; Ercolani, C.; Floris, B.; Bassetti, M.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1357. (b) Chambron, J. C.; Coudret, C.; Sauvage, J. P. *New J. Chem.* **1992**, 16, 361.
 18. Neuse, E. W.; Meirim, M. G.; Blom, N. F. *Organometallics* **1988**, 7, 2562.
 19. Shim, S. C.; Doh, C. H.; Woo, B. W.; Kim, H. S.; Huh, K. T.; Park, W. H.; Lee, H. J. *Mol. Catal.* **1990**, 62, L11.
 20. Tsuji, Y.; Yokoyama, Y.; Huh, K. T.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1987**, 60, 3456.
 21. Tsuji, Y.; Huh, T. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, 50, 1365.
 22. Brunet, J. J. *Chem. Rev.* **1990**, 90, 1041, and references therein.
 23. March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 834.
 24. Harada, K. In Patai, S. Ed., *The Chemistry of the Carbon-Nitrogen Double Bond*; Interscience: London, 1970; p 276.
 25. (a) Ball, G. E.; Cullen, W. R.; Fryzuk, M. D.; Henderson, W. J.; James, B. R. MacFarlane, K. S. *Inorg. Chem.* **1994**, 33, 1464. (b) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G. J.; Rettig, S. J. *Inorg. Chem.* **1991**, 30, 5002. (c) Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P.; Kang, G. J.; Herb, G.; Thorburn, I. S.; Spogliarich, R. J. *Mol. Catal.* **1990**, 62, 243. (d) Spindler, F.; Pugin, B.; Blaster, H.-U. *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 558. (e) Chan, Y. N. C.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, 112, 9400. (f) Longley, C. J.; Goodwin, T. J.; Wilkinson, G. *Polyhedron* **1986**, 5, 1625. (g) Vastag, S.; Bakos, J.; Toros, S.; Takach, N. E.; King, R. B.; Heil, B.; Marko, L. J. *Mol. Catal.* **1984**, 22, 283.
 26. (a) Cullen, W. R.; Kim, T. J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1983**, 2, 714. (b) Cullen, W. R.; Kim, T. J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1985**, 4, 346.

New Device for Addition of Modifier to Supercritical Fluid Carbon Dioxide Mobile Phase

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A new device to accurately deliver small amount of modifier into supercritical carbon dioxide fluid is described. Carbon dioxide, the most widely used mobile phase in supercritical fluid chromatography, is a relatively non-polar fluid, and hence the addition of small amount of polar modifiers could be necessary to migrate polar solutes. In this work, supercritical CO₂ and modifier are delivered from the pump to a 100 μ L mixing chamber in which a small magnetic bar is rotating. After passing through the mixing chamber, supercritical CO₂ is changed to a new mobile phase with different polarity. The amount of modifier added into supercritical CO₂ is measured by an amperometric microsensor, which is prepared from a thin film of perfluorosulfonate ionomer.

Introduction

In 1962, the idea of using dense gases for the transport of nonvolatile substances through a chromatographic column

was conceived and reduced to practice by Klesper *et al.*¹ in a simple chromatographic apparatus using porphyrins as the eluates. Many developments have been made since then, especially during the 1980s, supercritical fluid chromato-

graphy (SFC) has progressed from a laboratory curiosity to a viable analytical technique for solving many otherwise intractable problems.

Carbon dioxide is widely used as a primary mobile phase in SFC because of its low critical temperature, low toxicity, chemical inertness and nonflammability. However, because of its nonpolar nature,^{2,3} neat CO₂ is limited in its ability to elute polar compounds.

Therefore, a major objective of research into SFC has been directed towards increasing the range of solute polarity that can be handled by the technique. To bring the SFC technique into routine use, mobile phases that are more polar than the commonly used CO₂ are necessary. Polar mobile phases such as NH₃ exhibit useful properties,⁴ but a more practical way to extend the range of compounds separable by SFC is the use of mixed mobile phases. The addition of modifiers (generally organic solvents) to supercritical CO₂ changes the polarity of the mobile phase and also leads to a deactivation of the column packing material.⁵

Janssen and co-workers⁶ explained the effects of adding polar modifiers to supercritical fluid CO₂ mobile phase in three different ways: (A) increasing mobile phase polarity, (B) increasing mobile phase density, (C) deactivation of active sites on the surface of the stationary phase. In capillary SFC, most separations are carried out with pure CO₂ because of its compatibility with a flame-ionization detector (FID); indeed, except for formic acid and water the addition of any common modifier precludes the use of an FID.⁷ Although it is desirable to use FID in SFC, only water and formic acid produce acceptably low background noise and enable the use of this universal detector. Water and formic acid have been suggested by some investigators as very useful modifiers in packed column SFC^{8,9} because they significantly improve the separation of some polar compounds.

One of the simple and effective ways for the addition of modifiers to supercritical fluid mobile phase reported in the literature is to use a saturator column¹⁰ which is usually a silica column saturated with polar modifiers.

In our laboratory, μ -Porasil column¹¹ and highly porous stainless-steel filters^{12,13} which are saturated with polar modifiers have been used successfully as a modifier mixing device. One problem with these kinds of saturation type mixing devices is that the amount of polar modifiers dissolved in supercritical fluid CO₂ can not be changed easily because the principle of mixing is based on the saturation.

In this paper, a new mixing device is introduced, in which small mixing chamber with magnetic bar was used to generate water-modified carbon dioxide mobile phase. With this device, the amount of polar modifier (water) added can be changed easily by controlling the flow rate of modifier pump.

Experimental

A Micro-LC pump (Micro-Tech Scientific, Model Prodigix 4P) and Syringe pump (ISCO, Model 260D) were used to add modifier to supercritical fluid CO₂. SFC-grade carbon dioxide (Scott Specialty Gases) was used as a primary fluid and water (Fisher Scientific, Water-HPLC grade) was used as a modifier. The mixing device was manufactured in our laboratory through modification of Dynamix-

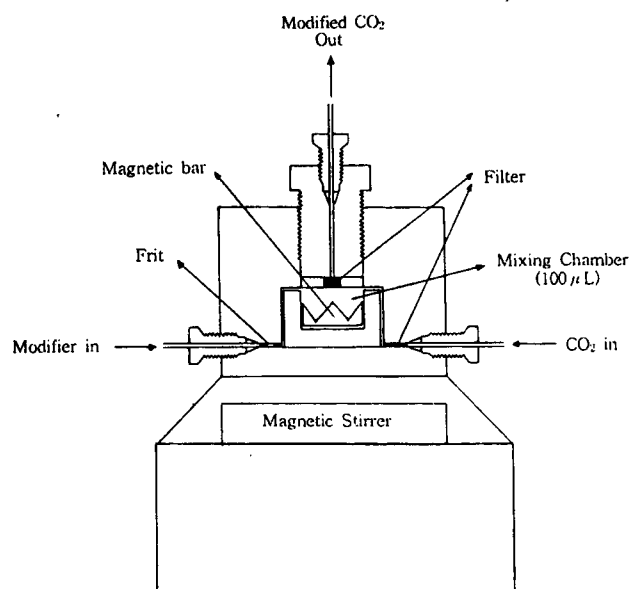


Figure 1. Mixing Device.

Plus mixer (Micro-Tech Scientific, Sunnyvale CA, USA).

Figure 1 shows the cross section of the mixing device developed in our laboratory. The characteristics of this mixing device are the following: (A) small volume of mixing chamber (100 μ L) (B) use of small magnetic bar for uniform mixing (C) use of a frit to add a small amount of modifier to supercritical fluid CO₂.

To measure the amount of modifier dissolved in the supercritical fluid, an amperometric microsensor was designed and made of perfluorosulphonate ionomer (PFSI).¹¹ A constant-current power supply (0.1 μ A) (Sungeun, Seoul, South Korea) was used to measure output was recorded on a strip-chart recorder (Knauer). Figure 2 shows the cross section of the modifier sensor used. Platinum wire was wrapped with PFSI thin film and another platinum wire was wound in a coil over the assembly. The sensor made in this way was placed in a plastic tube and the entire modifier measuring device was assembled as shown in Figure 3.

Figure 4 shows the overall schematic diagram of on-line modifier addition system using a new mixing device. Modifier is delivered to the mixing device by the Micro-LC pump and CO₂ is pressurized and delivered by Syringe pump.

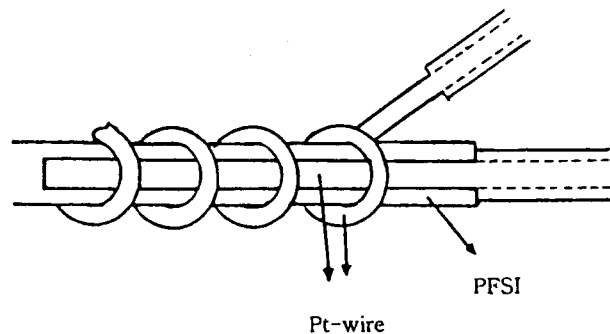


Figure 2. Modifier Sensor.

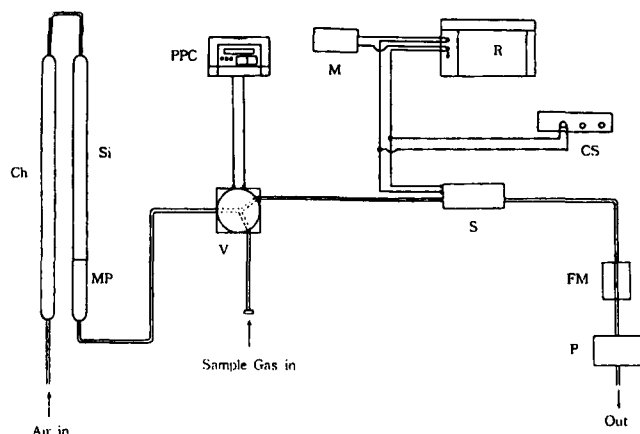


Figure 3. Schematic diagram of the mixing device used to measure water content: Ch, charcoal; Si, silica gel; MP, magnesium perchlorate; PPC, programmable process controller; V, solenoid valve; M, multimeter; R, recorder; CS, current source; S, sensor; FM, flow meter; P, pump.

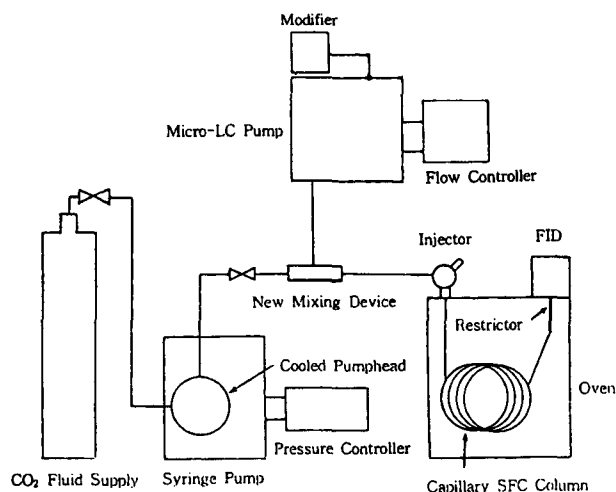


Figure 4. Schematic diagram of on-line modifier addition system using new mixing device.

Results and Discussion

Binary mobile phases can be obtained either by premixed cylinders or generated on-line during the chromatographic run. When dealing with premixed cylinders, it should be mentioned that some problems always arise. First, the gradual change in modifier concentration takes place in the premixed cylinder with time.¹⁴ Second, a binary mixture of eluents can contaminate the instrument. In particular, modifiers remaining in a pump can cause corrosion of the pump and be slowly eluted during the next run. This can affect the time required to achieve chemical equilibrium for the subsequent separations. Third, many modifiers can diffuse in the laboratory and contaminate the laboratory air. In our previous work,⁸ to overcome these problems, we used the μ -Porasil column which was saturated with a modifier and located between syringe pump and injector. Since a polar modifier (water) is added to the pressurized carbon dioxide fluid after the pump, no modifier remains in the pump.

When supercritical CO_2 passes through the μ -Porasil column, H_2O , retained on the $-\text{OH}$ groups of μ -Porasil by hydrogen bonding, can dissolve in the pressurized supercritical fluids. With this method, non-polar supercritical CO_2 can have the characteristics of a polar mobile phase because it can absorb polar solvent (H_2O). Therefore, after passing through the μ -Porasil column, supercritical CO_2 is changed to a new mobile phase with different polarity, and it is possible to separate polar samples using this new mobile phase. However, when dealing with the use of μ -Porasil column, we found a serious problem always arise. The problem was a bad reproducibility of the amount of modifier dissolved in the supercritical carbon dioxide. When the same experiments were repeated several times, it was very difficult to obtain reproducible results in the chromatograms since the amount of modifier in the mobile phase does not remain constant with time. For these reason, another mixing device^{12,13} was developed, in which high porous stainless steel filters which are manufactured for in-line filters for HPLC were used to hold a large amount of water. While in the μ -Porasil column water can be held on the stationary phase by hydrogen bonding, with this device water can be held physically inside small pores of filters. After being saturated with water, the device is also placed between a pump and an injector. With this design, supercritical CO_2 is delivered from the pump to the device which is saturated with water. When supercritical CO_2 goes through the device, water held within the small pores of the filter can be dissolved in the pressurized supercritical fluids.

These mixing devices mentioned above were very successful to generate modified mobile phase for SFC. However, with these kinds of mixing devices, we can not change the amount of modifier added in supercritical CO_2 . This is a serious drawback of these devices since the amount of modifier added into supercritical mobile phase could change mobile phase polarity and mobile phase density which is crucial for the separation of polar compounds.

For these reasons, we tried to develop a new type of modifier mixing device (Figure 1). In Figure 1, a small volume of mixing chamber (100 μL) and a magnetic bar were used to allow rapid equilibration of the CO_2 /water mixture. a frit (2 cm $\times$ 0.3 mm i.d.) was also utilized to inject a small amount of water into the mixing chamber. Using the described modifier mixing device, 0.2%-1.2% water mixture could be generated without problems (Figure 8). The amount of water added can be controlled by changing the flow rate of Micro-LC pump and the pressure of supercritical CO_2 .

To measure the amount of water dissolved in supercritical CO_2 after the new mixing device, a modifier sensor¹¹ which consists of a polymer film¹⁵ i.e. film of a perfluorosulfonate ionomer (PFSI) was used. PFSI polymer has high affinity for water. When PFSI film was in contact with two electrodes and a constant current flows through the film, the water that partitions into the film from the surrounding environment was electrolytically decomposed. The change of voltage across two electrodes was used as a measure of the water content of the environment surrounding the sensor. The resistance of PFSI film was changed according to the water content of supercritical CO_2 fluid and the voltage difference between two Pt-wire was recorded and measured.

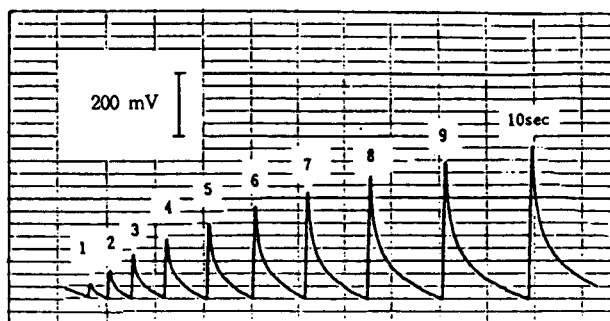


Figure 5. Relative peak heights at different time intervals for air saturated with water.

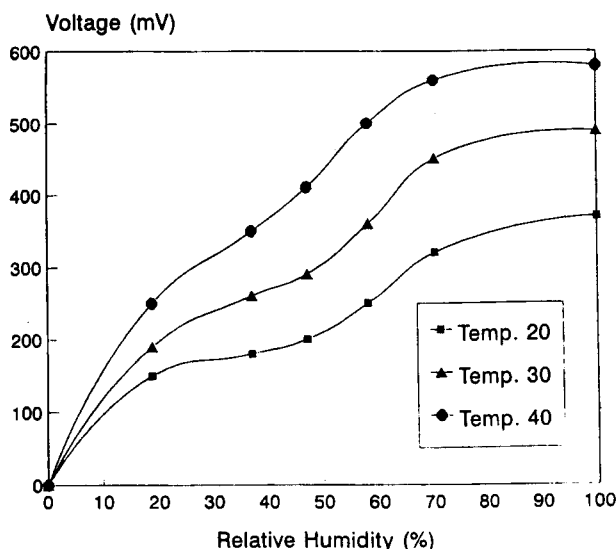


Figure 6. Sensor response with various relative humidity levels. (18.8%, 37.1%, 47.2%, 58.3%, 70.4%, 100% RH)

Graphs in Figure 6 were used as standard curves in which the sensor outputs were measured with six different standard relative humidity streams on various temperature. H_2SO_4 solutions of known composition¹⁶ was used to generate the standard relative humidity streams. Figure 5 shows the relative peak heights at different time interval for air saturated with water. Air saturated with water was generated by passing air, with bubbling, through water contained in two sequential bottles, and was injected directly into the sensor.

It is interesting to note that the amount of water added into the supercritical CO_2 at the pressure of 2000 psi is less than at 1500 psi (Figure 7). This can be explained in the following: high pressure of supercritical CO_2 fluid results in the high pressure of the mixing chamber, and the pressure of the mixing chamber prevents modifier from flowing into the mixing chamber. In another words, the pressure of the mixing chamber works as a back-pressure for the delivery of modifier by Micro-LC pump.

In our laboratory, the SFC separations of polar samples using this new mixing device will be studied extensively in the near future. The new mixing device developed in this work is simple, convenient, and reliable, and should contribute to progress in various studies on modified su-

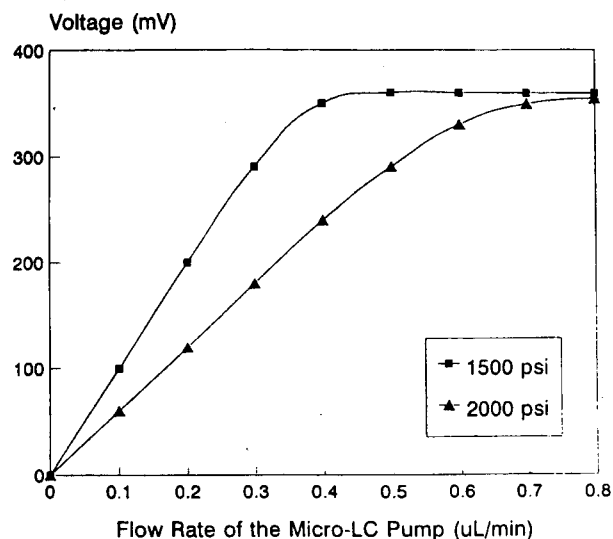


Figure 7. Plots of the sensor response versus various flow rate of the Micro-LC pump.

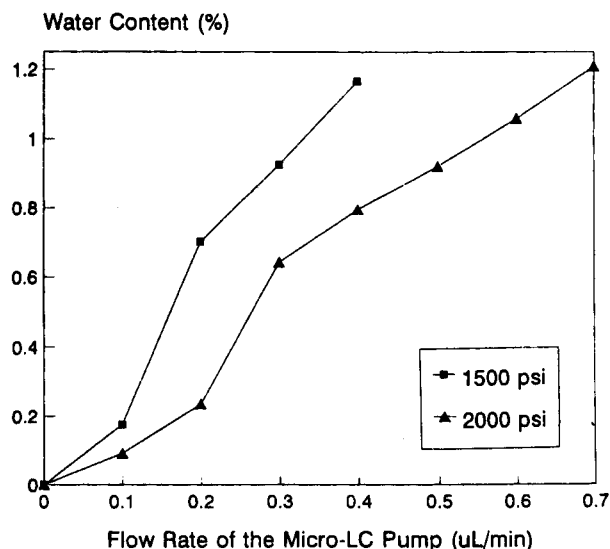


Figure 8. Measurements of the water content in supercritical CO_2 at various flow rate of Micro-LC pump.

percritical fluid chromatography.

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References

1. Klesper, E.; Corwin, A. H.; Turner, D. A. *J. Org. Chem.* **1962**, *27*, 700.
2. Hyatt, J. A. *J. Org. Chem.* **1984**, *49*, 5097.
3. Yonker, C. R.; Frye, S. L.; Lalkwarf, D. R.; Smith, R. D. *J. Phys. Chem.* **1986**, *90*, 3002.
4. Kuei, J. C.; Markides, K. E.; Lee, M. L. *J. High Resolut. Chromatogr.* **1987**, *10*, 257.
5. Blilie, A. L.; Greibrokk, T. *Anal. Chem.* **1985**, *57*, 2239.
6. Janssen, J. G. M.; Scheenmakers, P. J.; Cramers, C. A.

- J. High Resolut. Chromatogr.* **1989**, 12, 645.
7. Wright, B. W.; Smith, R. D. *J. Chromatogr.* **1986**, 355, 367.
 8. Pyo, D.; Ju, D. *The Analyst* **1993**, 118, 253.
 9. Schwartz, H. E.; Barthel, P. J.; Moring, S. E.; Yates, T. L.; Lauer, H. H. *Fresenius Z. Anal. Chem.* **1988**, 330, 204.
 10. Engelhardt, H.; Gross, A.; Mertens, R.; Petersen, M. J. *Chromatogr.* **1989**, 477, 169.
 11. Pyo, D.; Hwang, H. *Anal. Chim. Acta* **1993**, 280, 103.
 12. Pyo, D.; Ju, D. *Chromatographia* **1994**, 38, 79.
 13. Pyo, D.; Ju, D. *Analytical Sciences* **1994**, 10, 171.
 14. Weerd, M. D.; Dewaele, C.; Verzele, M.; Sandra, P. J. *High Resolut. Chromatogr.* **1990**, 13, 40.

FT-IR Spectroscopic Study of Preparation of Lead Zirconium Titanate (PZT) by Sol-Gel Processing

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Gelation time, gel structure and volatility of by-products during gelation of PZT sol-gel processing were investigated by FT-IR spectroscopy. FT-IR spectroscopic study was performed on PZT gels with the various H₂O contents (1, 2 and 3 mol) and the several types (HNO₃, NH₄OH) and amounts (0.1, 0.2 mol) of catalysts, monitoring temporal (0, 1, 3, 10 weeks, 3 months and 3 years) and thermal (100-700 °C) changes of FT-IR spectra. The interpretation of temporal change of the spectra revealed two trends. One is under the condition of 1 mol H₂O, 1 mol H₂O+0.1 mol HNO₃, 3 mol H₂O and the other is for 1 mol H₂O+0.1 mol NH₄OH, 2 mol H₂O, 1 mol H₂O+0.2 mol HNO₃. The gel structures and the gelation times for these conditions were discussed in comparison with the reported results of SiO₂, and we suggested the reaction mechanisms for these structural characteristics. Thermal variation of FT-IR spectra was interpreted as the evolution processes of gel by investigating the evaporation of solvent and the decomposition of organic residues.

Introduction

An increasing attention has been focused in last few years on ferroelectric thin films for the potential applications of electronic and electro-optic devices, which can be used as pyroelectric sensors,¹ non-volatile memories,² substrate materials for surface acoustic wave (SAW) elements,³ decoupling capacitors⁴ and ferroelectric gate field-effect-transistors (FETS).⁵ These devices employ ferroelectric thin films such as Pb(Zr,Ti)O₃, (Pb,Lu)(Zr,Ti)O₃, PbTiO₃, BaTiO₃, KNbO₃, (Sr,Ba)Nb₂O₆, (Pb,Ba)Nb₂O₆.⁶⁻⁸ In the present study, the gelation process of PZT, prepared by a sol-gel processing for the thin films, was investigated with the FT-IR spectra of PZT gels under various different conditions. That is, the evaporation of solvent and/or by-products, and the structure and gelation time of PZT gel were studied. The composition of PZT was chosen to be Pb(Zr_{0.52}Ti_{0.48})O₃, the morphotropic boundary (MPB) of rhombohedral and tetragonal structure. It is well known that PZT shows optimized dielectric properties at this composition by the dielectric constant, polarization, piezoelectricity and SAW propagation.^{9,10}

PZT thin films have been fabricated using highly equipment-dependent vacuum deposition technique, such as

RF sputtering,^{11,12} ion beam deposition,¹³ electron beam evaporation,¹⁴ but these techniques are very costly and hard to obtain the stoichiometric composition of PZT thin films. Sol-gel processing, on the contrary, provides remarkable advantages such as low-cost, high purity, high homogeneity, low temperature synthesis and versatile formation of various shapes. Sol-gel processing is a chemical method based on inorganic polymerization of appropriate precursors in organic or inorganic solvent.¹⁵ Thin film of PZT can be fabricated by coating a stock solution on substrates using spin coater or dip coater, and by subsequent pyrolysis to promote polymerization, to remove solvent and to decompose organic residues, and by final heat treatment to form desired perovskite structure.

The properties of sol-gel derived PZT powders or thin films are closely related to the structure of gel, while gel structure depends on the amount of H₂O and the catalyst (type, amount) used in gelation process.¹⁶⁻¹⁸ Therefore, we studied in this paper the progress of PZT gelation with various H₂O contents (1, 2 and 3 mol) and the several types (HNO₃, NH₄OH) and amounts (0.1, 0.2 mol) of catalysts, by monitoring temporal (0, 1, 3, 10 weeks, 3 months, 3 years) and thermal (100-700 °C) changes of FT-IR spectra. The structure of polymer and the evaporation of solvent and/or by-products and the gelation time were discussed with peak positions and shifts of the FT-IR spectra.

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