용액법을 이용한 $Pb(Mg_{1/3}Nb_{2/3})O_3$의 합성

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Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ by Solution Method

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국문요약

$Pb(Mg_{1/3}Nb_{2/3})O_3$은 높은 유전율과 전기저항 및 유전율의 온도변화율이 적은 Pb계 relaxor의 대표적인 재료로서 적층 세라믹 콘덴서 재료에의 응용이 크게 기대되고 있다. 그러나 산화물 분말을 이용하는 일반적인 세라믹스 합성방법으로는 $Pb(Mg_{1/3}Nb_{2/3})O_3$의 단일상의 합성이 어렵고, 합성과정에서 저유전율상인 pyrochlore상이 공존하여 $Pb(Mg_{1/3}Nb_{2/3})O_3$의 전기적 특성을 저하시킨다.

본연구에서는 용액을 이용하여 $Pb(Mg_{1/3}Nb_{2/3})O_3$의 단일상을 합성하고자 하였다. 출발물질로는 값싼 금속염인 Niobium Oxalate, Magnesium Nitrate 및 Lead Nitrate를 선정하고 증류수에 용해하여 혼합용액을 제조하고, 합성방법으로는 초음파 분무 열분해법과 에멀젼법을 이용하였다. 초음파 분무 열분해법에서는 750℃에서 합성한 분말을 다시 750℃에서 하소하여 $Pb(Mg_{1/3}Nb_{2/3})O_3$ 단일상을 합성할 수 있었으며, 에멀젼법에서는 800℃에서 $Pb(Mg_{1/3}Nb_{2/3})O_3$ 단일상을 합성할 수 있었다.

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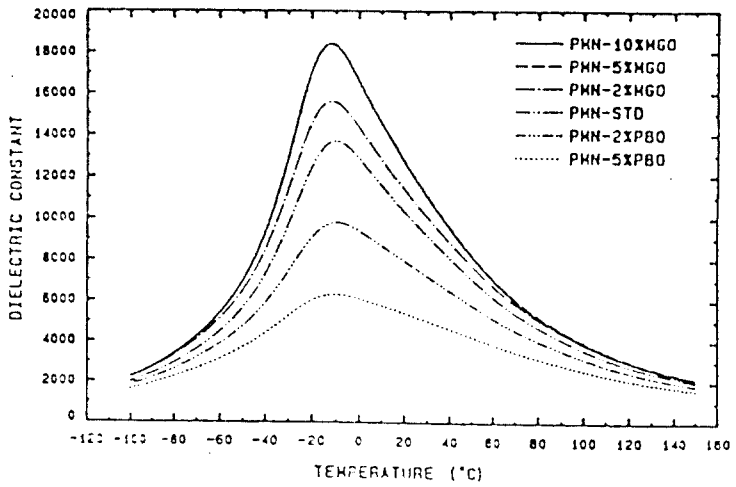
$Pb(Mg_{1/3}Nb_{2/3})O_3(PMN)$

Lead containing Lelaxor Ferroelectrics

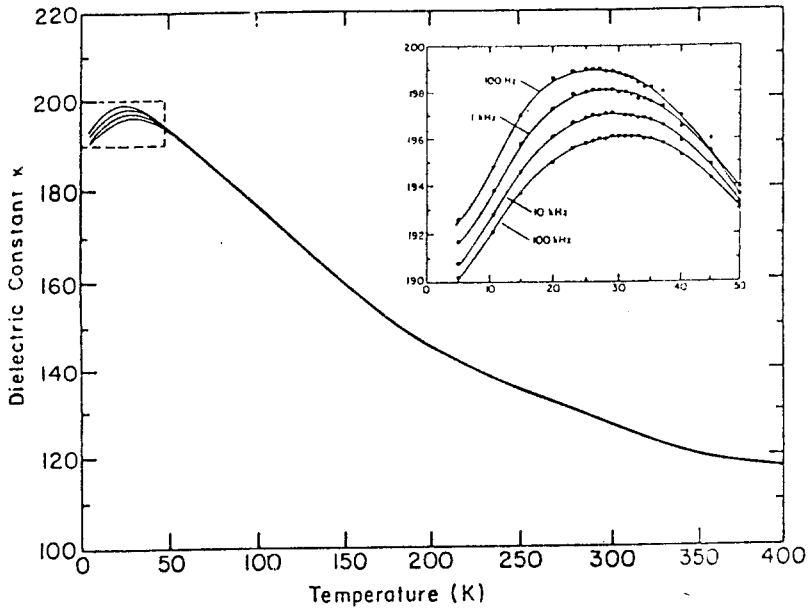
1. Broad Dielectric Constant changed with Temperature
2. High dielectric constant and resistivity
3. Low Sintering Temperature

⇒ Promising materials for ceramic multilayer capacitor



Pyrochlore by Shrout

1. Composition : $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$
2. Dielectric Constant



PMN Formation Reacrion by Inada

$$3PbO + 2Nb_2O_5 \xrightarrow{530\text{-}650^{\circ}C} 3PbO \cdot 2Nb_2O_5 \quad \text{(cubic pyrochlore)}$$

$$3PbO \cdot 2Nb_2O_5 + PbO \xrightarrow{600\text{-}700^{\circ}C} 2(2PbO \cdot Nb_2O_5) \quad \text{(rhombohedral pyrochlore)}$$

$$2PbO \cdot Nb_2O_5 + 1/3MgO \xrightarrow{700\text{-}800^{\circ}C} Pb(Mg_{1/3}Nb_{2/3})O_3 + 1/3(3PbO \cdot 2Nb_2O_5)$$

PMN Formation Reacrion by Swartz

$$PbO + Nb_2O_5 + MgO \xrightarrow{25\text{-}650^{\circ}C} \text{no reaction}$$

$$PbO + Nb_2O_5 + (MgO) \xrightarrow{700\text{-}800^{\circ}C} \text{cubic pyrochlore}$$

$$\text{Pyrochlore} + PbO + MgO \xrightarrow{850\text{-}900^{\circ}C} \text{perovskite} + \text{pyrochlore}$$

Pyrochlore Formation Reacrion by Decomposition

$$\text{Perovskite}[Pb(Mg_{1/3}Nb_{2/3})O_3] \xrightarrow{\text{above } 700^{\circ}C} \text{Pyrochlore} + PbO(\text{vapor}) + Mg_2Nb_4O_9$$

- PbO vaporization at the surface of sintered body
  - ⇒ Formation of Pyrochlore and $Mg_2Nb_4O_9$
  - ⇒ Lowering Diclectric Constant

Noble PMN Fabrication Technique

$$MgO + Nb_2O_5 \xrightarrow{1000^\circ C} MgNb_2O_6 \text{ (coumbite)}$$

$$MgNb_2O_6 + 3PbO \xrightarrow{800^\circ C} 3PMN$$

Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ Powder by Spray Pyrolysis with Ultrasonic Atomizer

Ultrasonic Spray Pyrolysis

Starting material : Precursor solution
Fine droplets
Rapid pyrolysis
Spherical particles

PMN Synthesis by Sol-Gel Process

Starting materials : Lead Acetate, $Pb(CH_3COO)_2 \cdot 3H_2O$

Magnsium Ethoxide, $Mg(OC_2H_5)_2$

Niobium Ethoxide, $Nb(OC_2H_5)_5$

Refluxing Condition : 125℃, 12hrs

Cryatal Phase : 775℃, 2hrs ⇒ 98% perovskite

Table 1. Selection of inorganic salt.

		$NbCl_5$ + HCl
Pb	$Pb(CH_3COO)_2$	×
	$Pb(NO_3)_2$	×
	PbO_2	○
Mg	$MgCl_2$	○

		$Nb(HC_2O_4)_5$ + HNO_3
Pb	$Pb(NO_3)_2$	○
Mg	$Mg(NO_3)_2$	○

○ Clear solution、× Precipitation

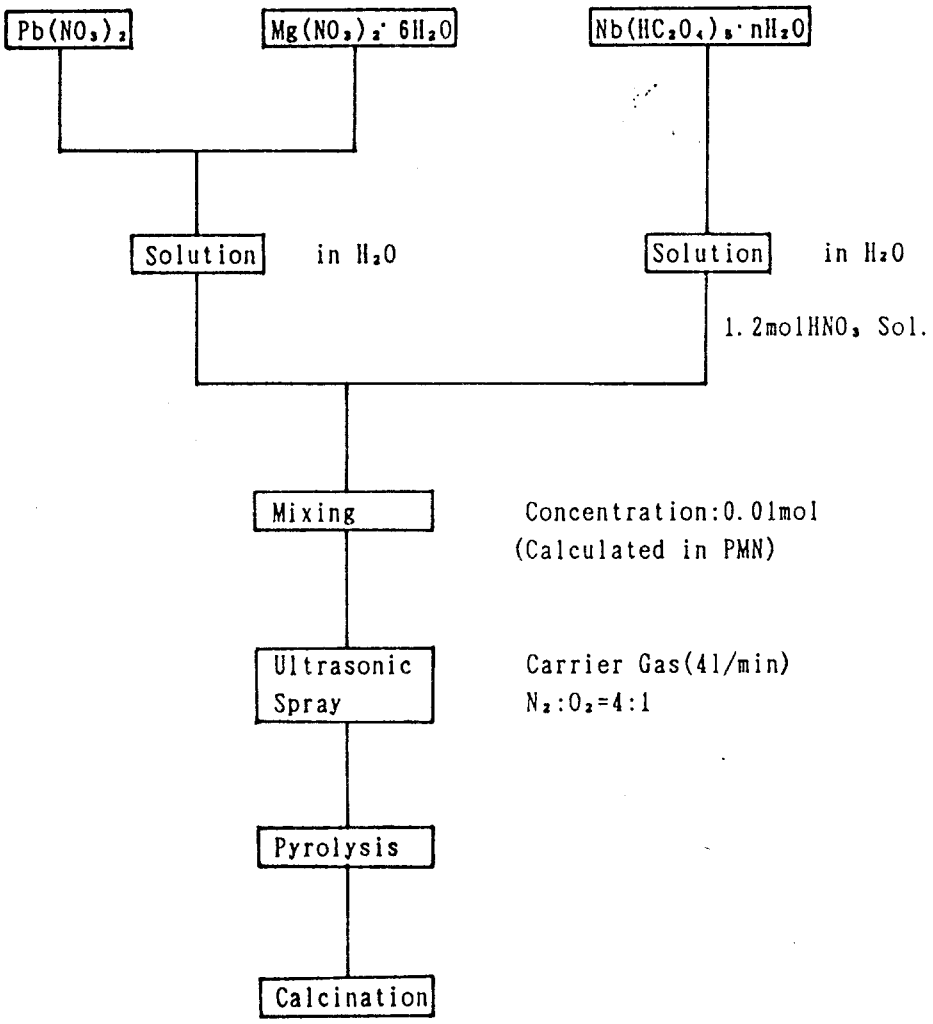


Fig. Flow sheet of experiment.

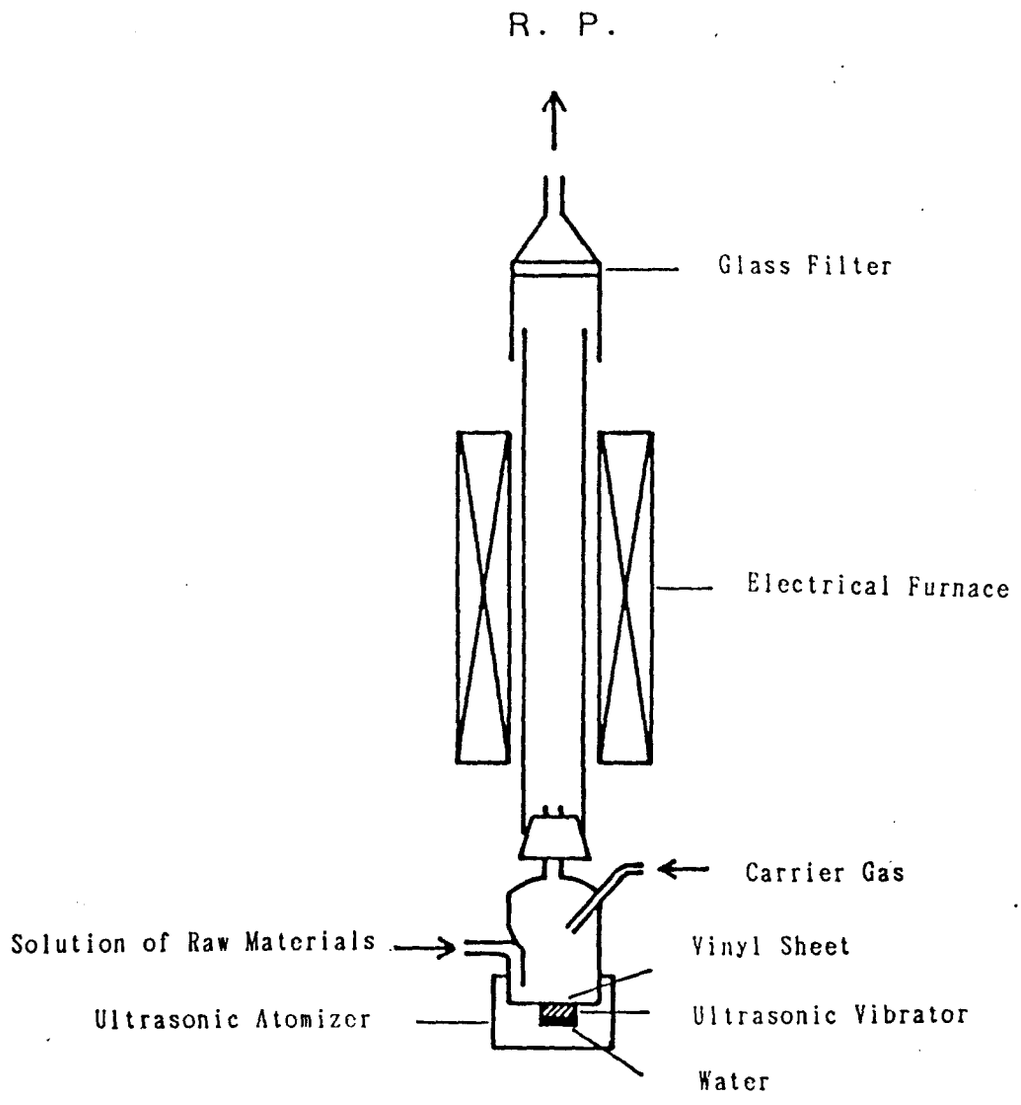


Fig. Schematic diagram of the ultrasonic spray pyrolysis apparatus.

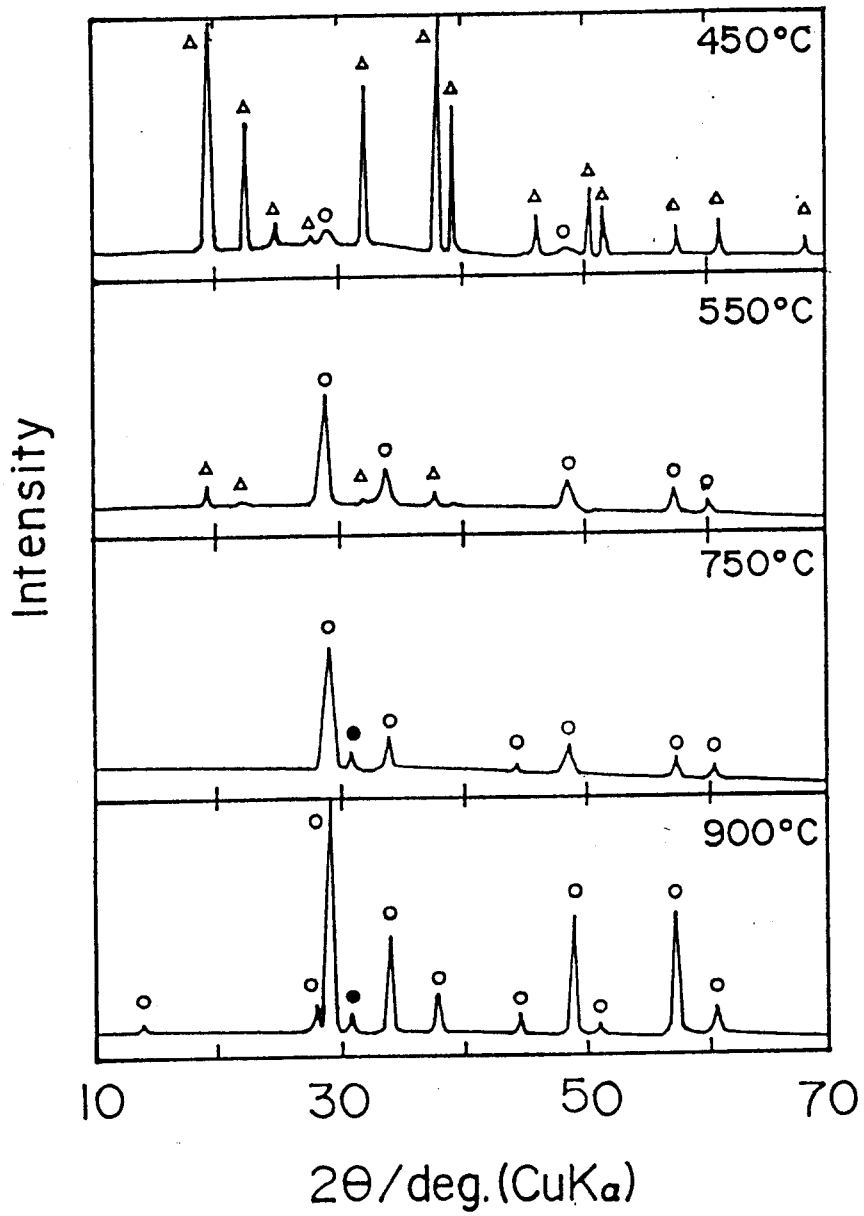


Fig. 1. XRD patterns of pyrolyzed powder at various temperature. ● PMN、
○ Pyrochlore、△ $Pb(NO_3)_2$

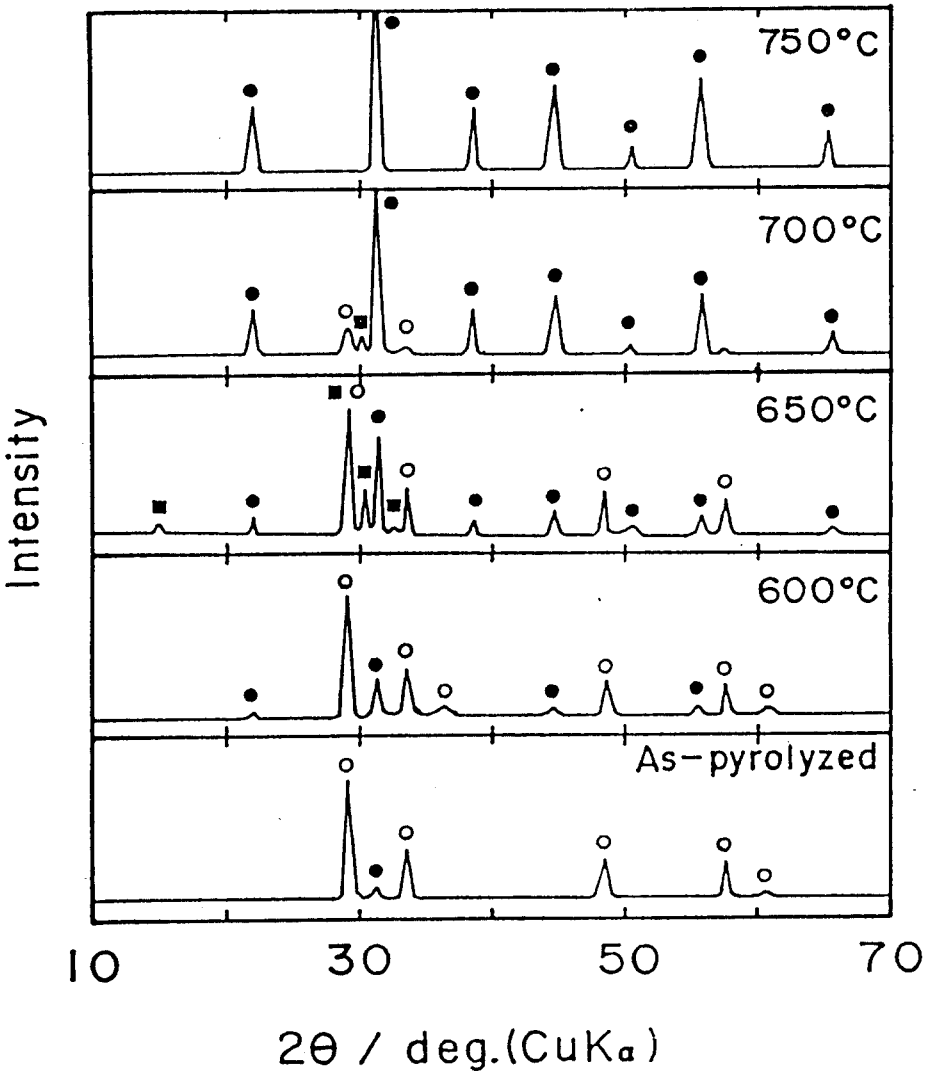


Fig. 2. XRD patterns of powder calcined at various temperature. ● PMN, ○ Pyrochlore, ■ PbO

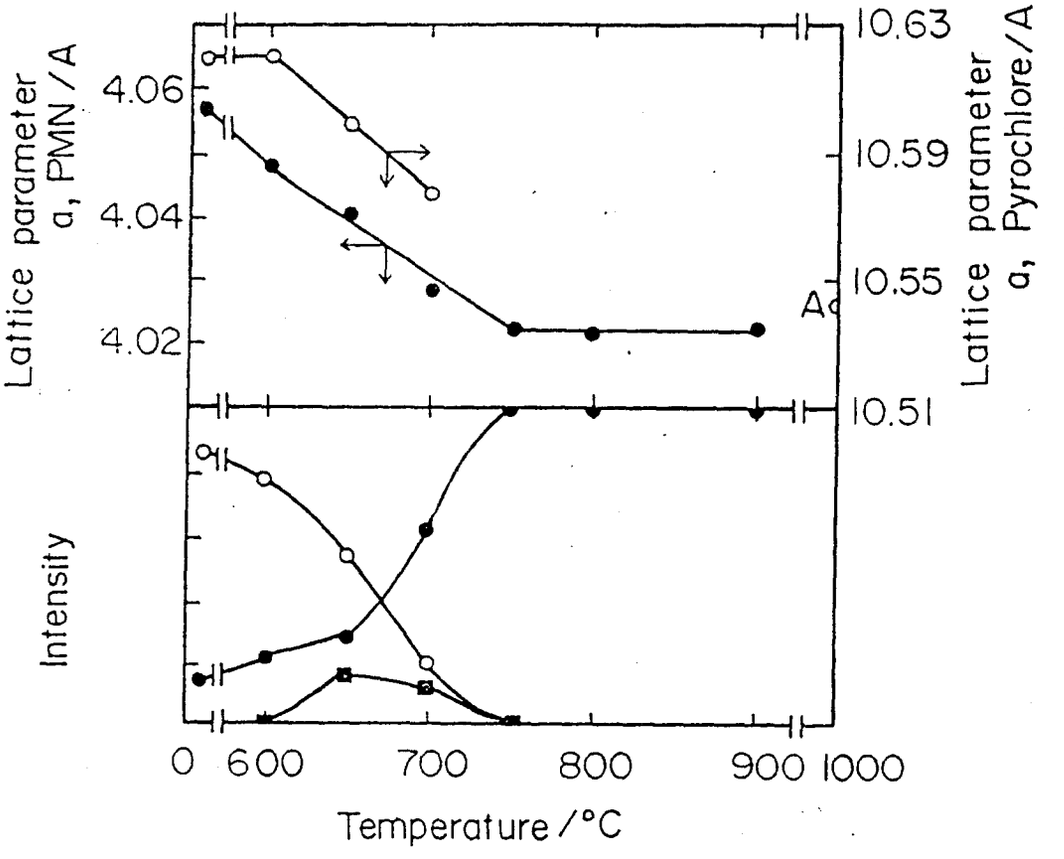


Fig. 3. Variations of lattice parameter and intensity of XRD of calcined powder at various temperatur
● PMN、○ Pyrochlore, ■ PbO

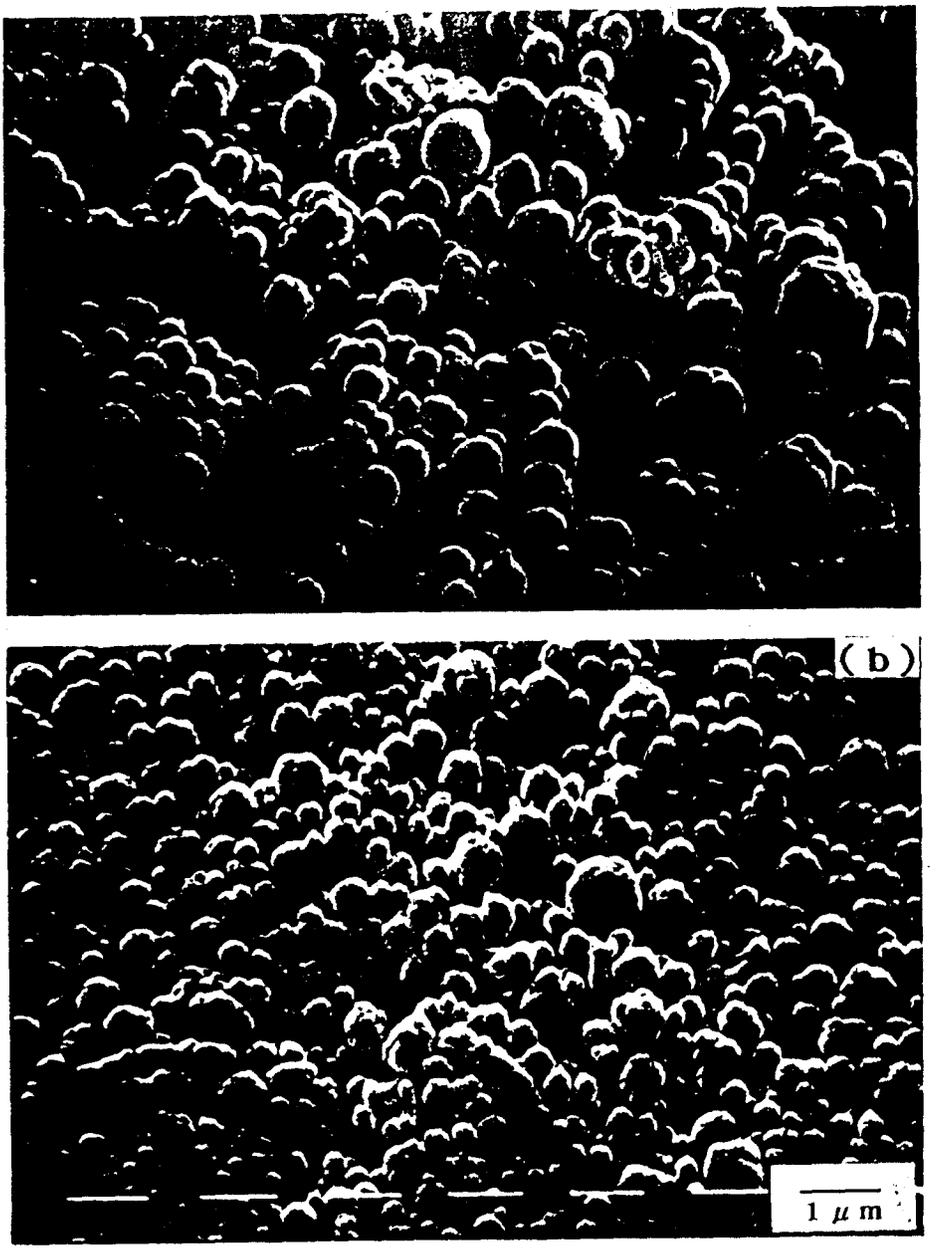


Fig. 4. SEM photographs of powders.
(a) Pyrolyzed, (b) Calcined at 750℃.

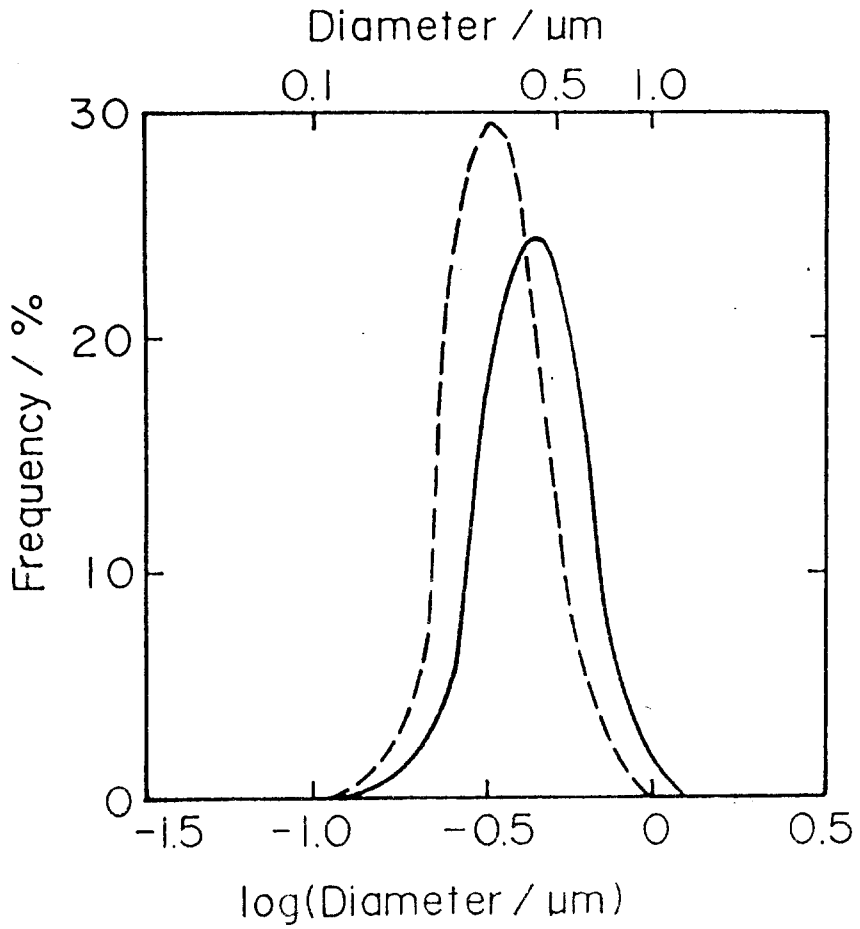


Fig. 5. Particle size distributions of powders.
——— Pyrolyzed, - Calcined at 750℃

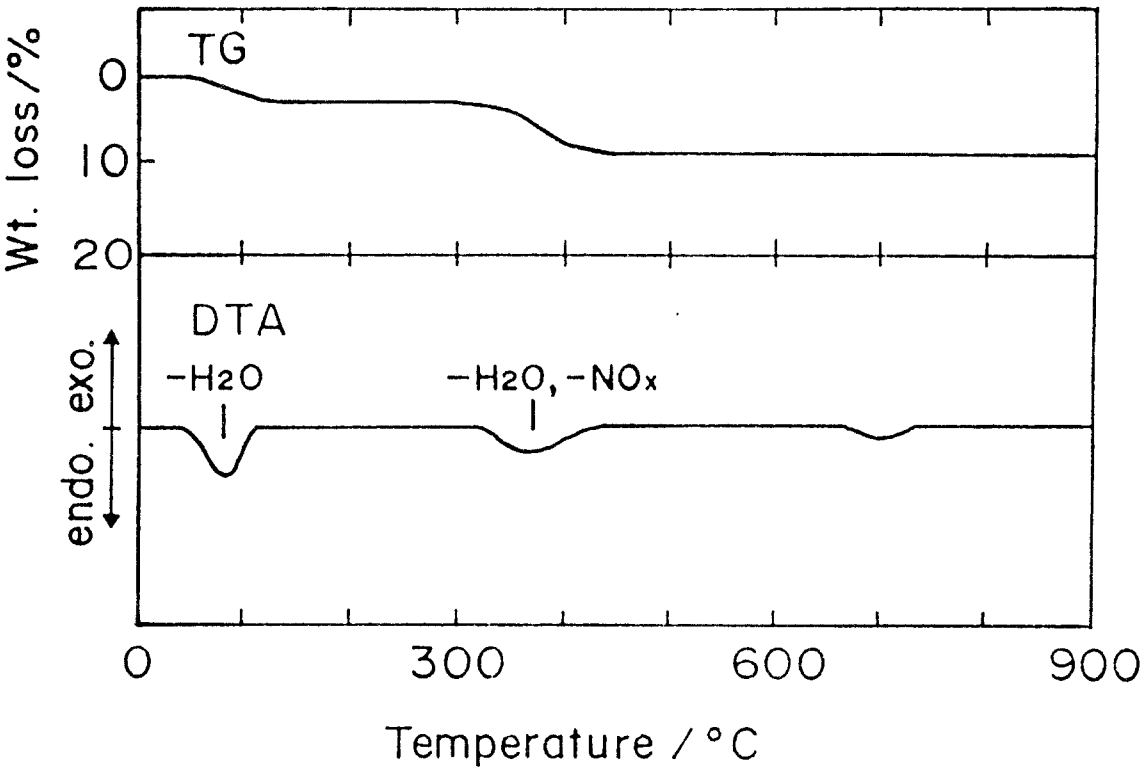


Fig. 6. DTA-TG curves of pyrolyzed powder.

Fig. 7. SEM photograph of fracture surface sintered at 900℃ for 5hrs.

Conclusion

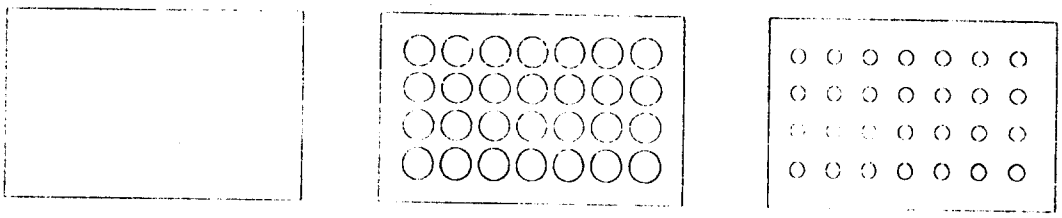
PMN was synthesized by ultrasonic spray pyrolysis and the results are as follows.

1. Lead nitrate, magnesium nitrate and niobium oxalate as raw materials were choosen and dissolved into distilled water with nitric acid.
2. The obtained powders by ultrasonic spray pyrolysis at 750℃ consist of mainly pyrochlore and little PMN. Single phase PMN powders were obtained by calcination of as pyroyzed powders at 750℃.
3. The particles had spherical shape with narrow size distribution and an average size of 0.36㎛.

Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ Powder by Emulsion Method

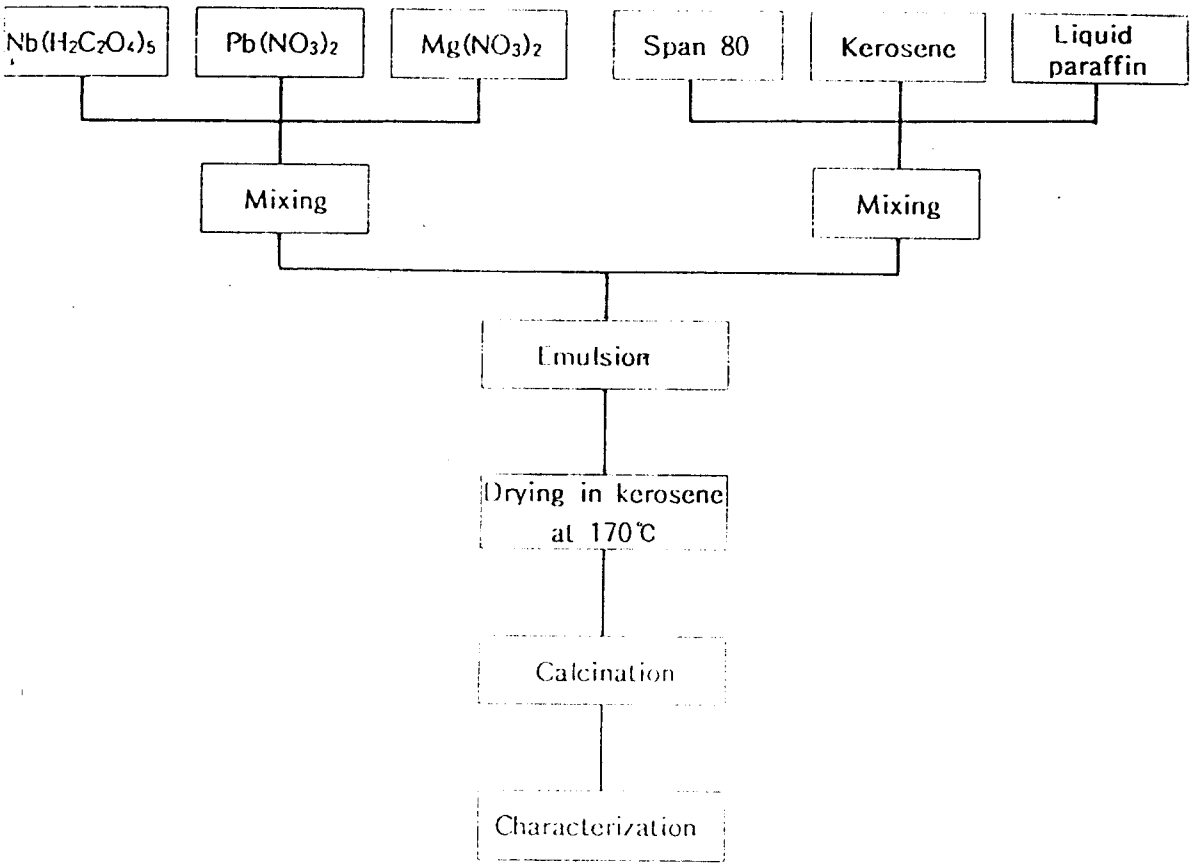
One step process to synthesize $Pb(Mg_{1/3}Nb_{2/3})O_3$

- Starting solution : Precursor solution
- Emulsion with organic phase



용액의 혼합　　원료용액+유기상　　에멀션

실험공정도



에멀젼의 현미경 사진

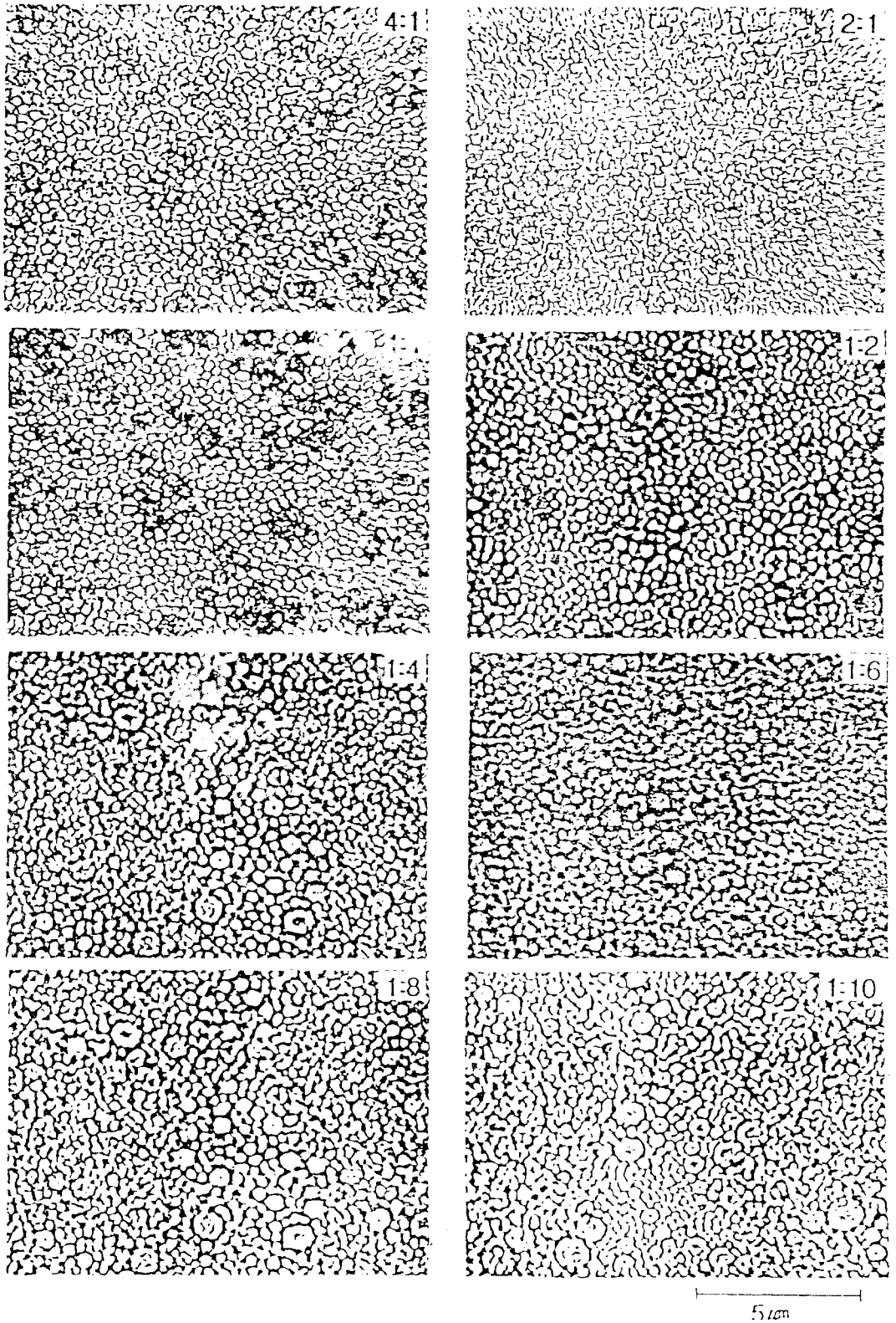
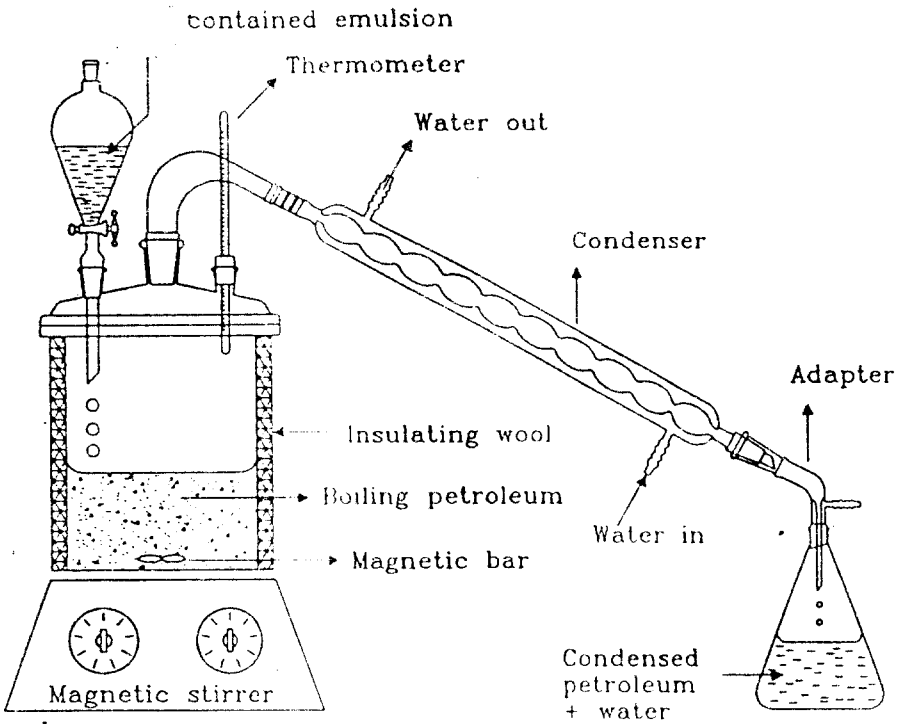


Fig. 1. Change of emulsion size with variation of ratio of organic phase to mixed solution.


contained emulsion
Thermometer
Water out
Condenser
Adapter
Insulating wool
Boiling petroleum
Magnetic bar
Water in
Magnetic stirrer
Condensed
petroleum
+ water

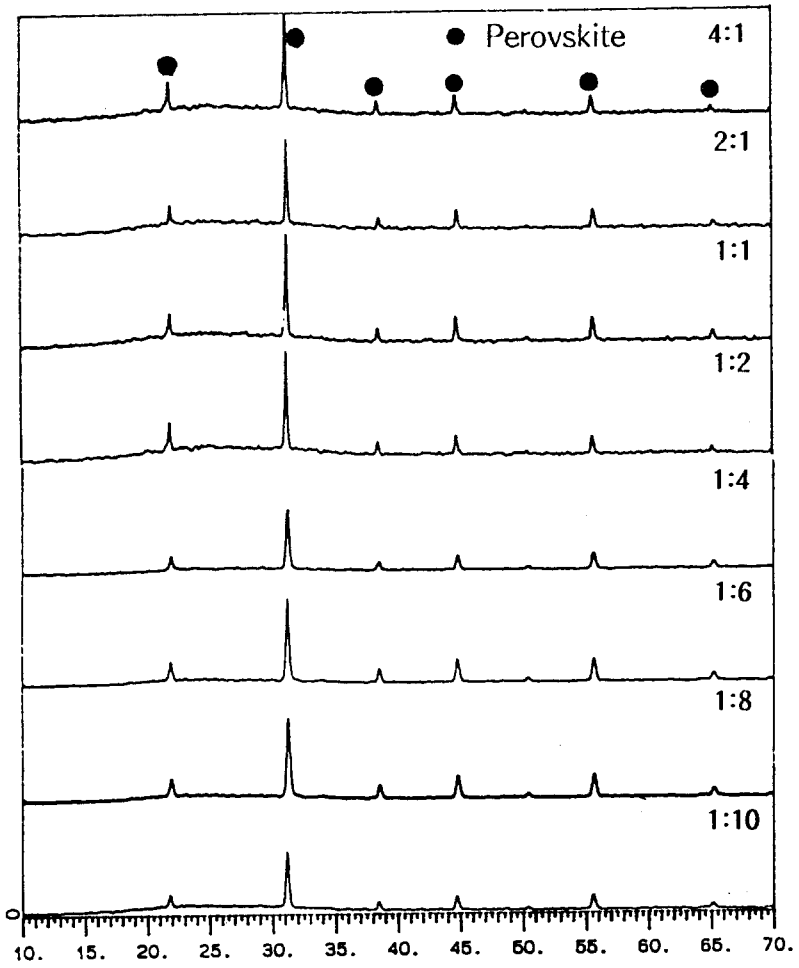


Fig. XRD patterns of powders prepared with various ratio of organic phase to mixed solution and calcined at 800℃.

건조분말의 열분석

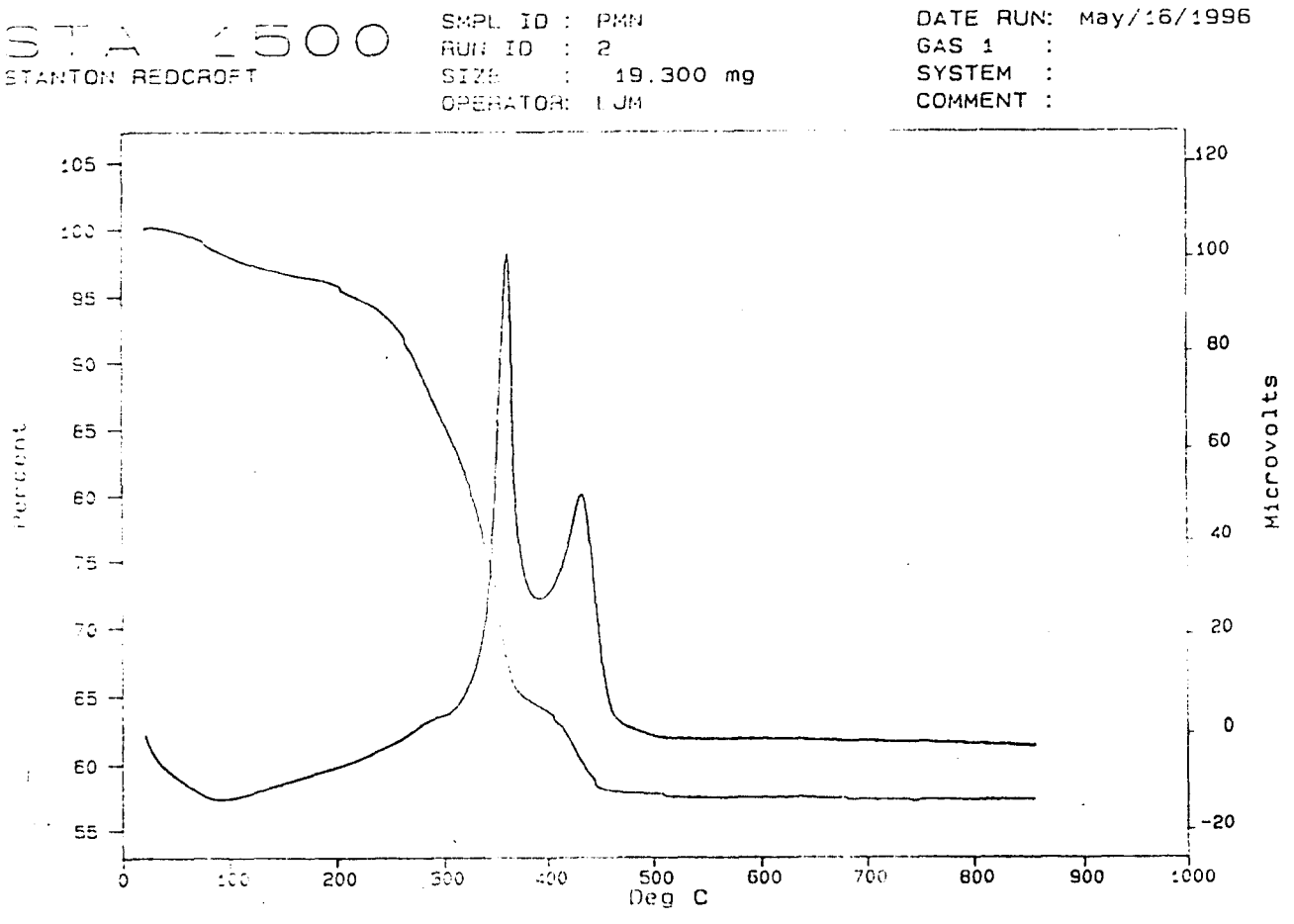
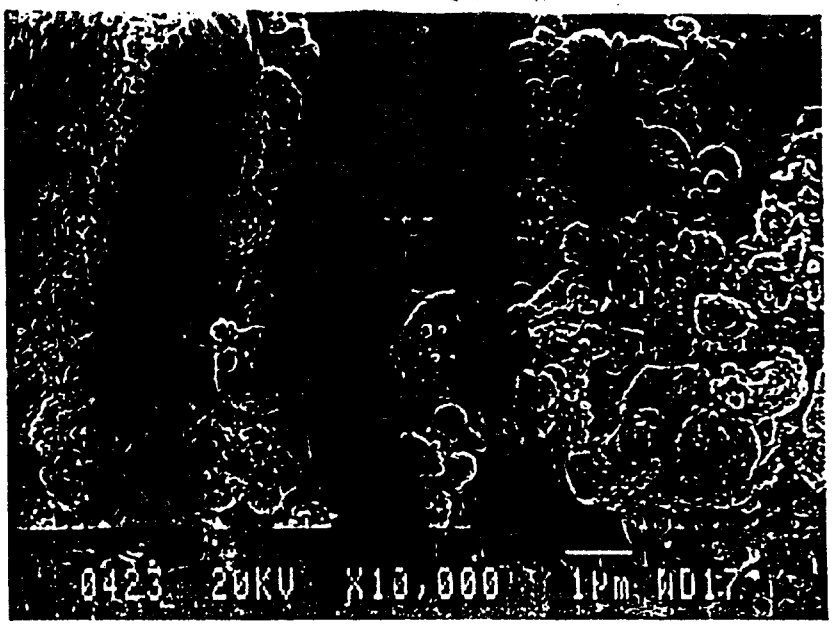
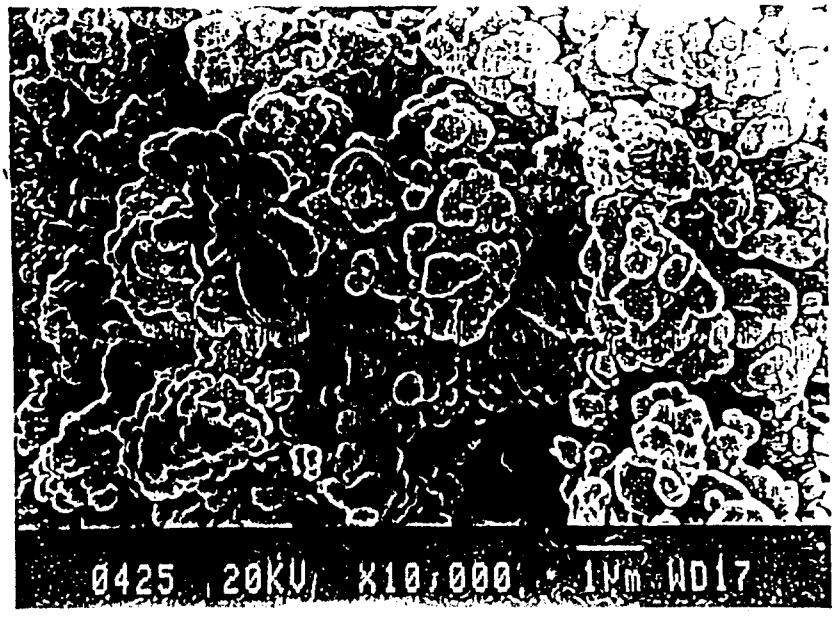


Fig. 2. DT-TGA curve of dryed powder in the ratio of organic phase to mixed solution, 1:2.



(a) SEM photograph of dryed powders prepared by emulsion method.



(b) SEM photograph of calcined powders at 800℃.

하소온도 변화에 따른 XRD

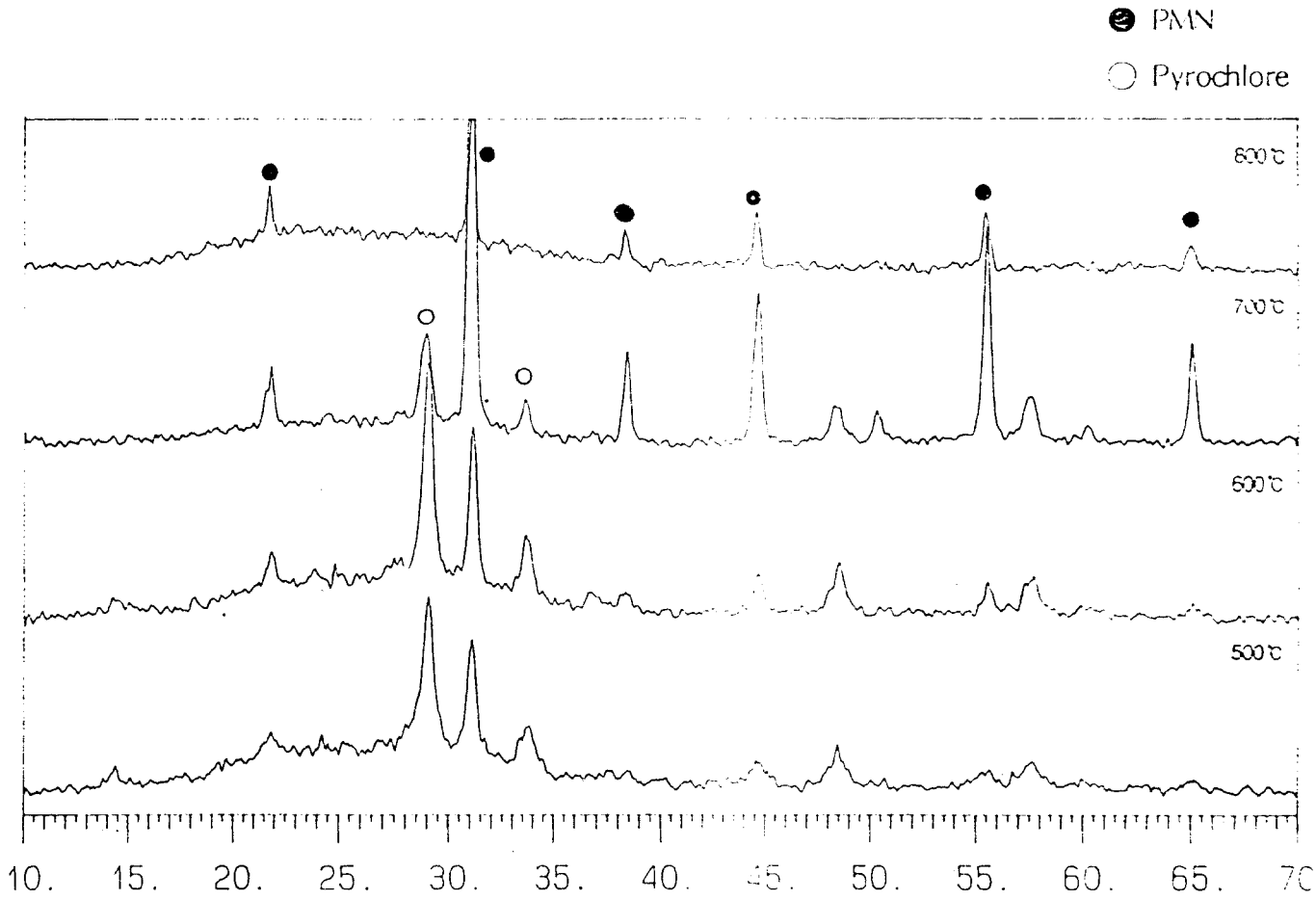


Fig. 3. X-ray diffractions of the powder heated at various temperatures prepared in the ratio of organic phase to mixed solution, 1:2

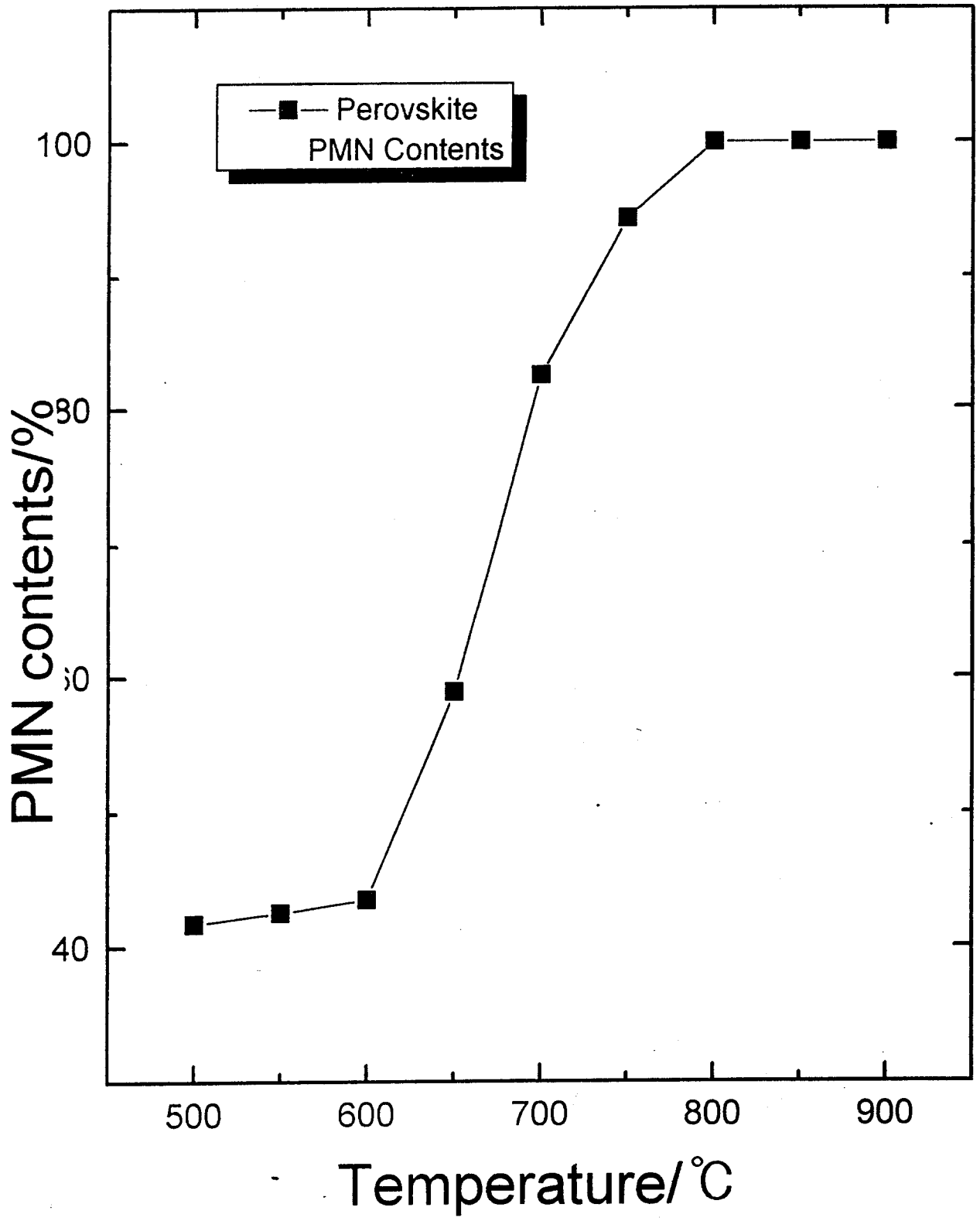
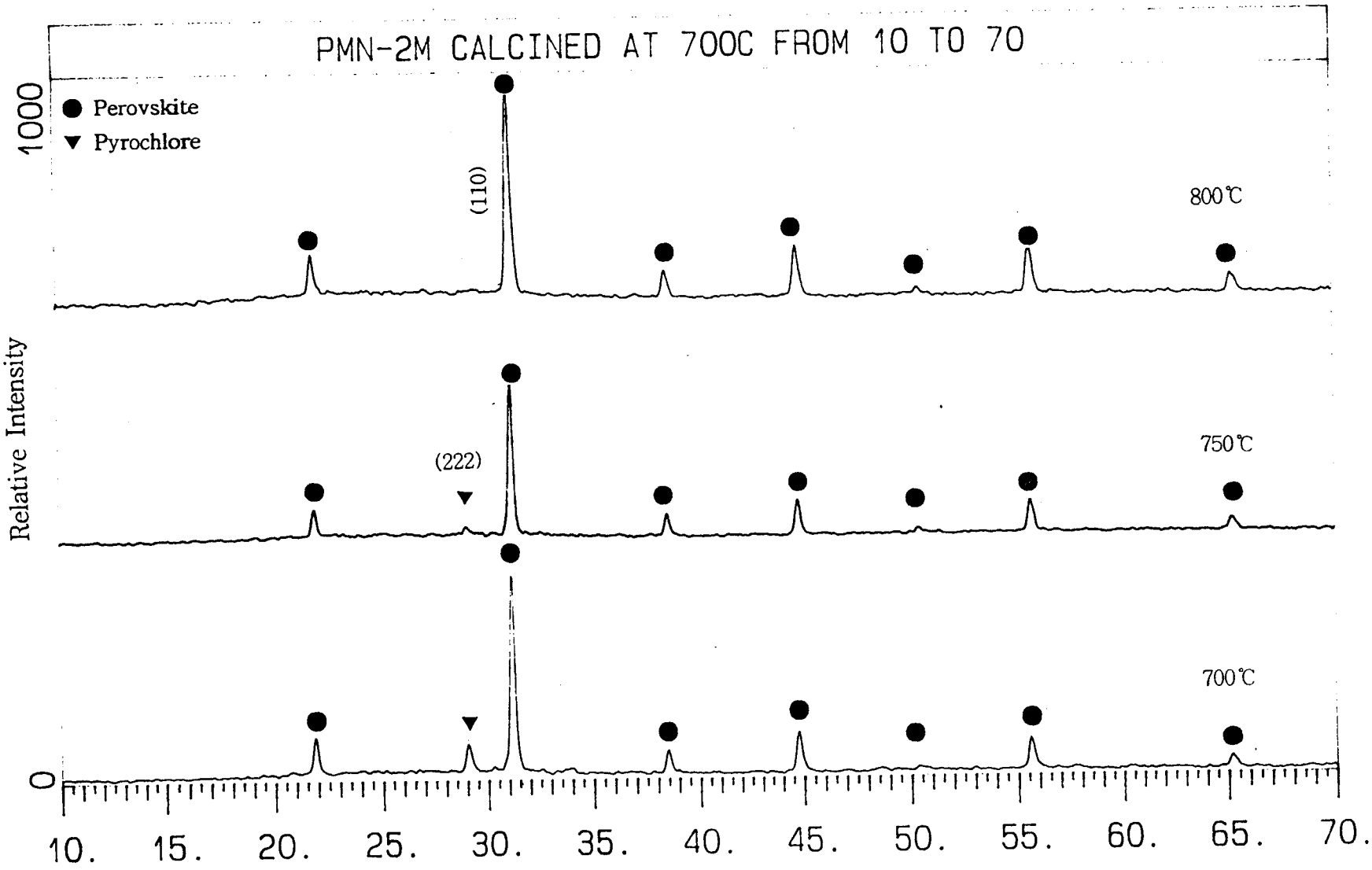


Fig. PMN contents of the stoichiometric PMN powders calcined at various temperatures.


PMN-2M CALCINED AT 700C FROM 10 TO 70
1000
Perovskite
Pyrochlore
(110)
800℃
(222)
750℃
700℃
Relative Intensity
0
10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60. 65. 70.

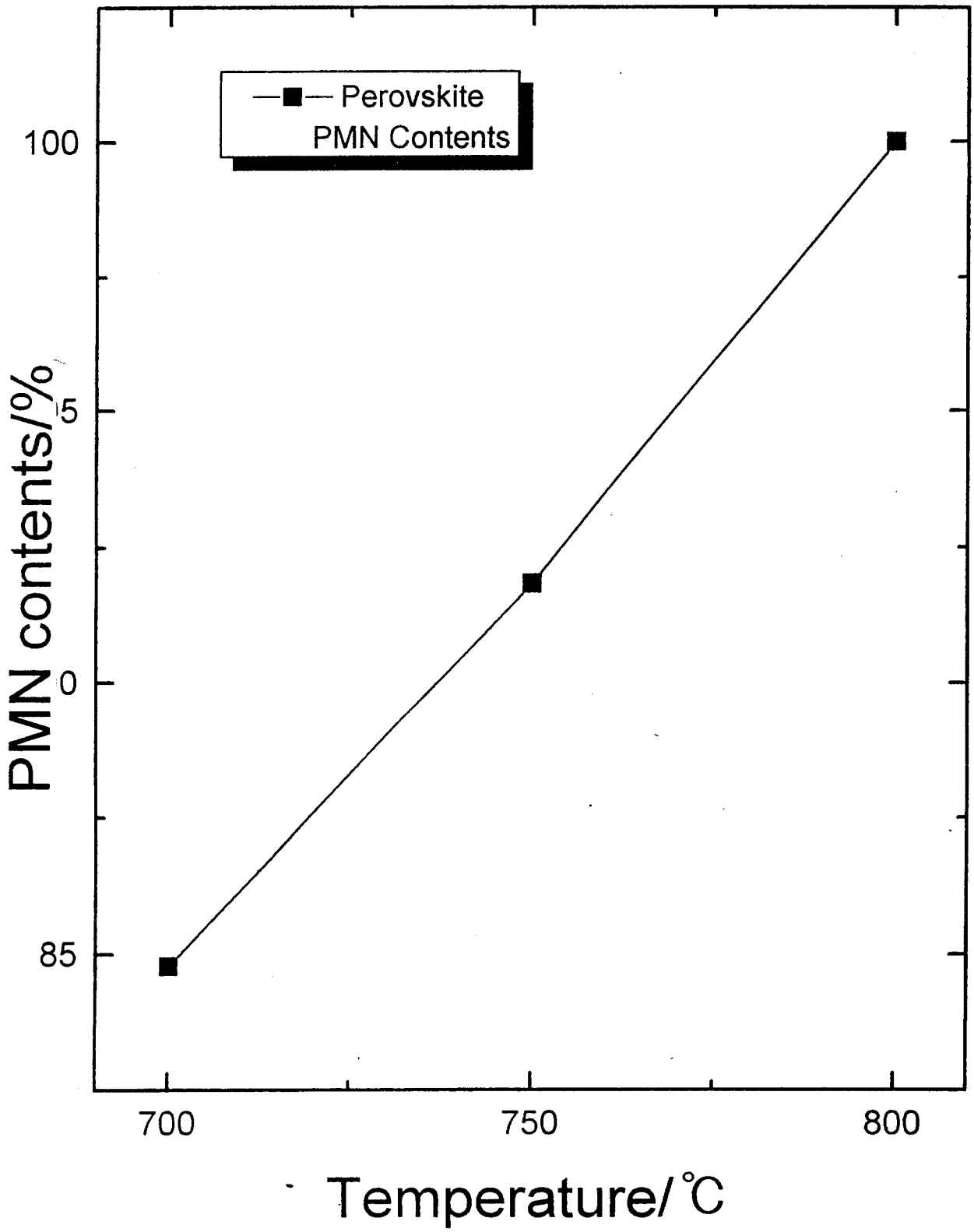
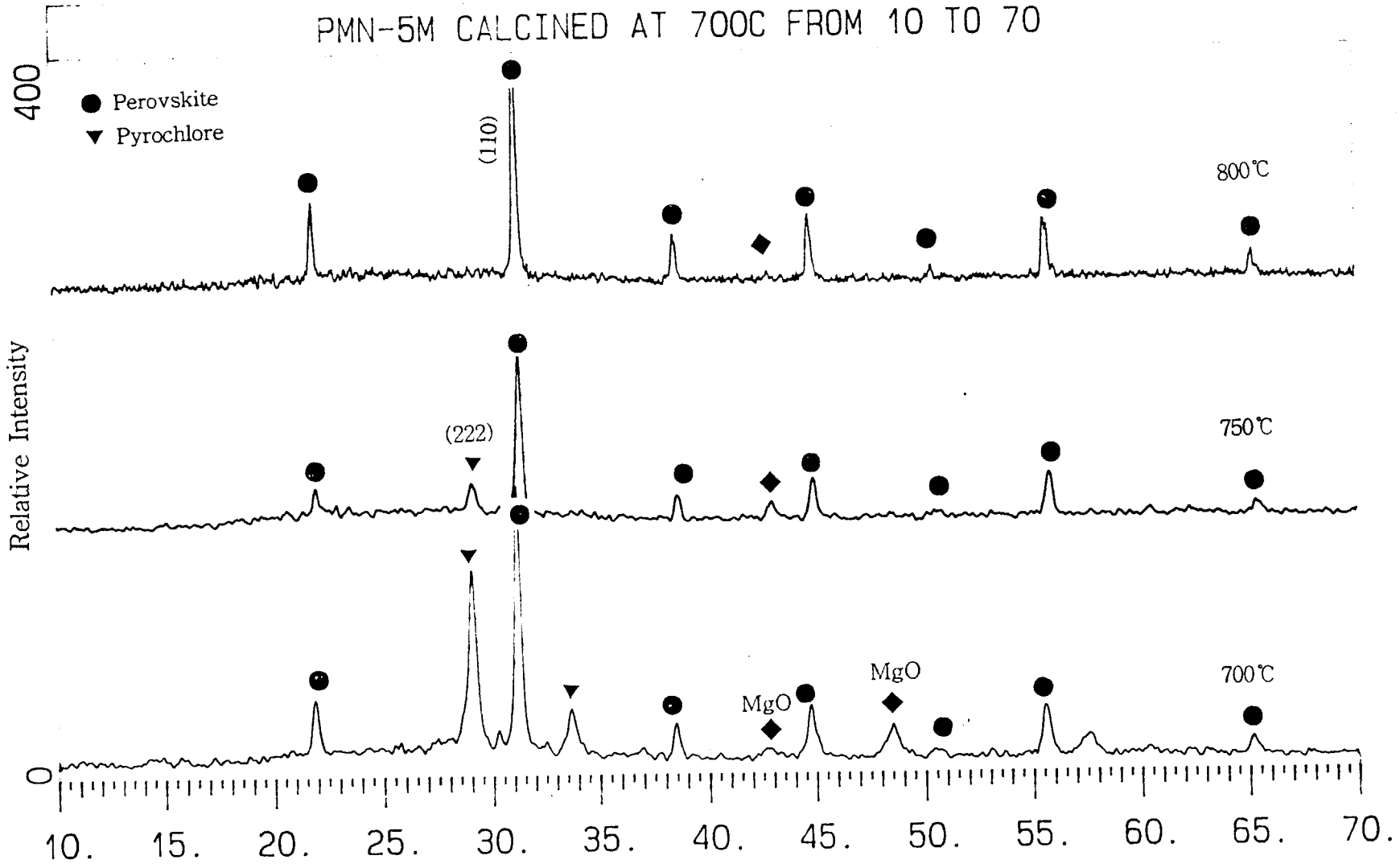


Fig. PMN contents of the powders with 2mol% excess MgO calcined at various temperatures.


PMN-5M CALCINED AT 700C FROM 10 TO 70
400
Perovskite
Pyrochlore
(110)
800℃
Relative Intensity
(222)
750℃
MgO
MgO
700℃
0
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
65.
70.

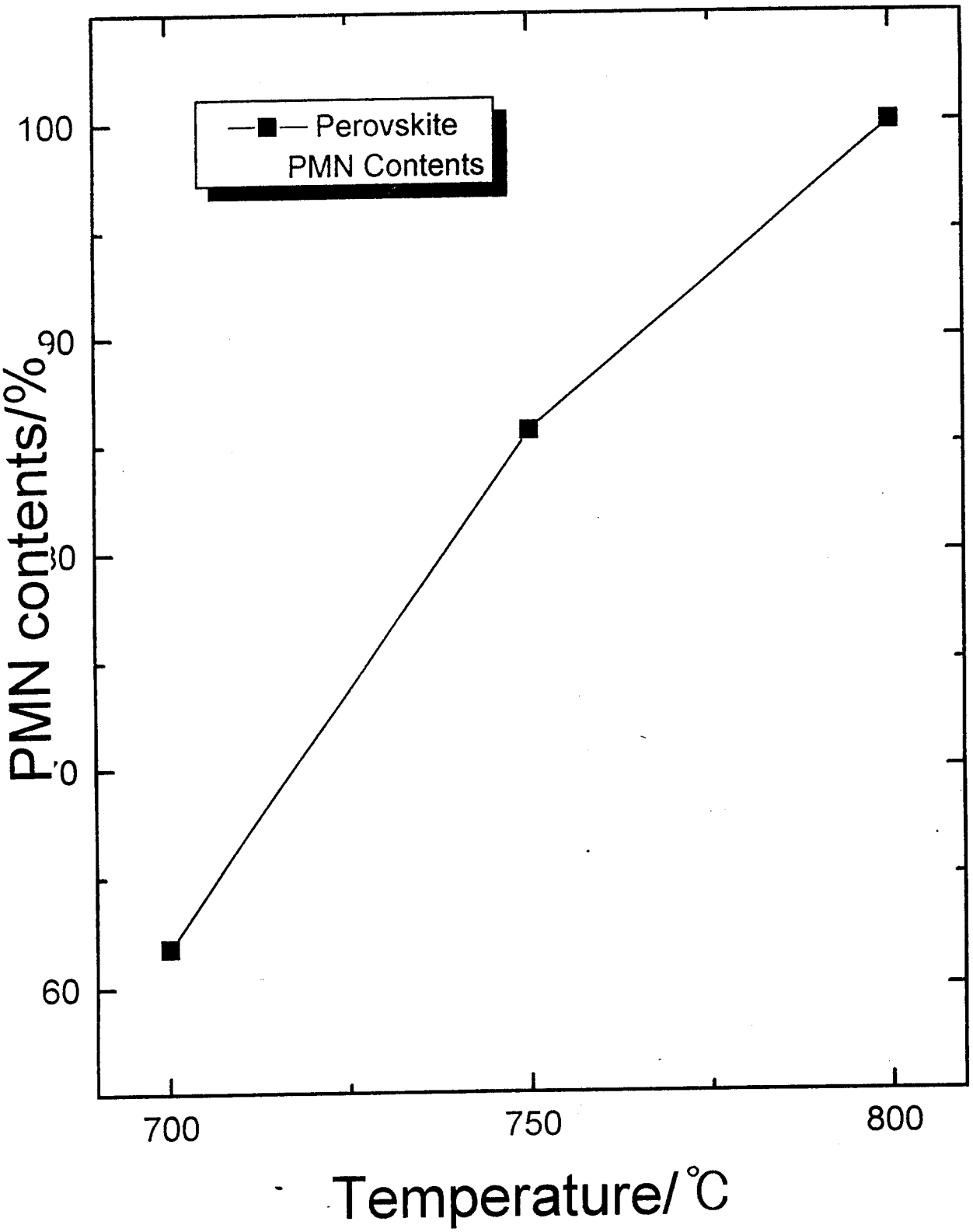
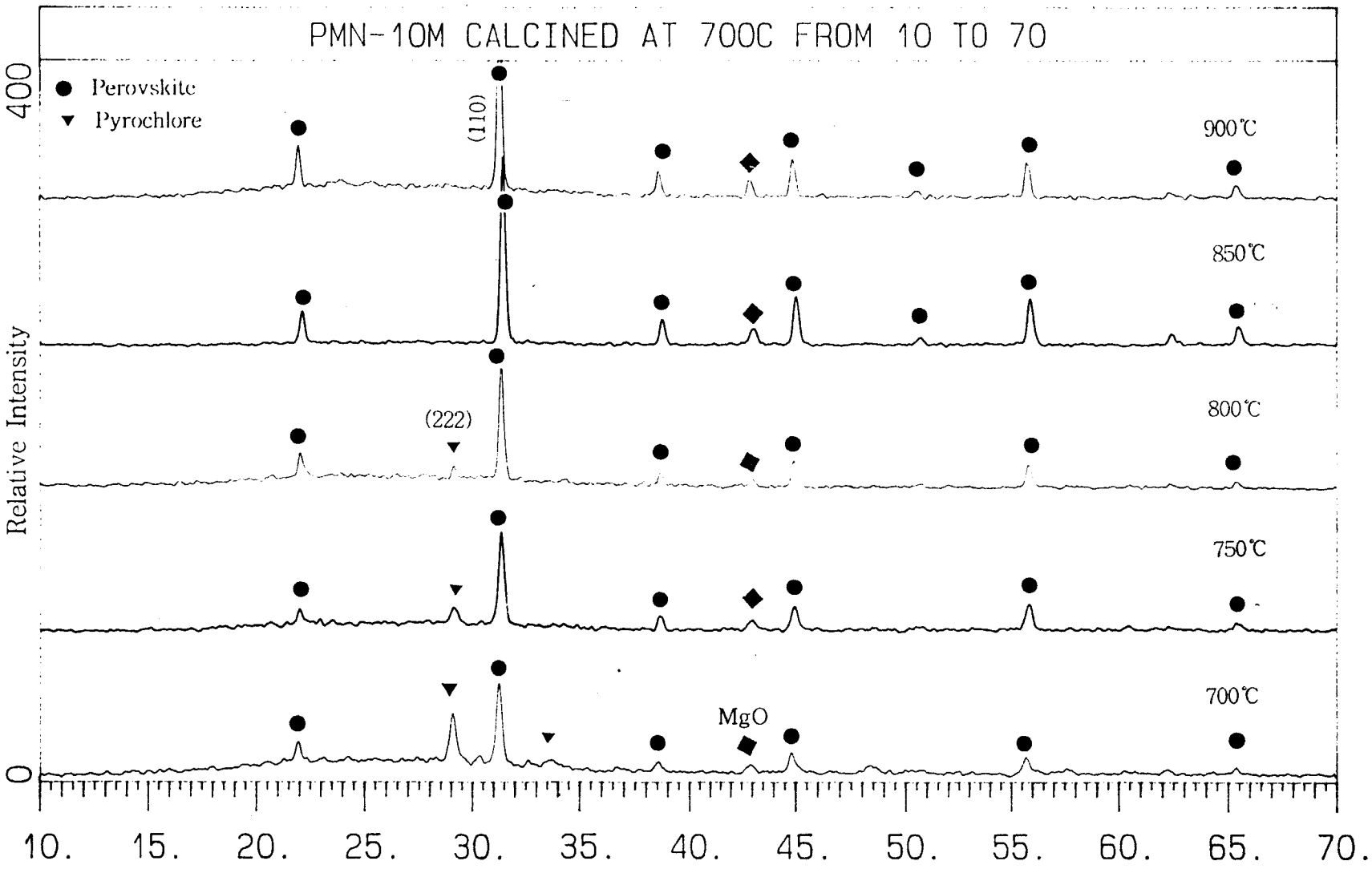


Fig. PMN contents of the powders with 5mol% excess MgO calcined at various temperatures.


PMN-10M CALCINED AT 700C FROM 10 TO 70
400
0
Relative Intensity
● Perovskite
▼ Pyrochlore
(110)
(222)
MgO
900℃
850℃
800℃
750℃
700℃
10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60. 65. 70.

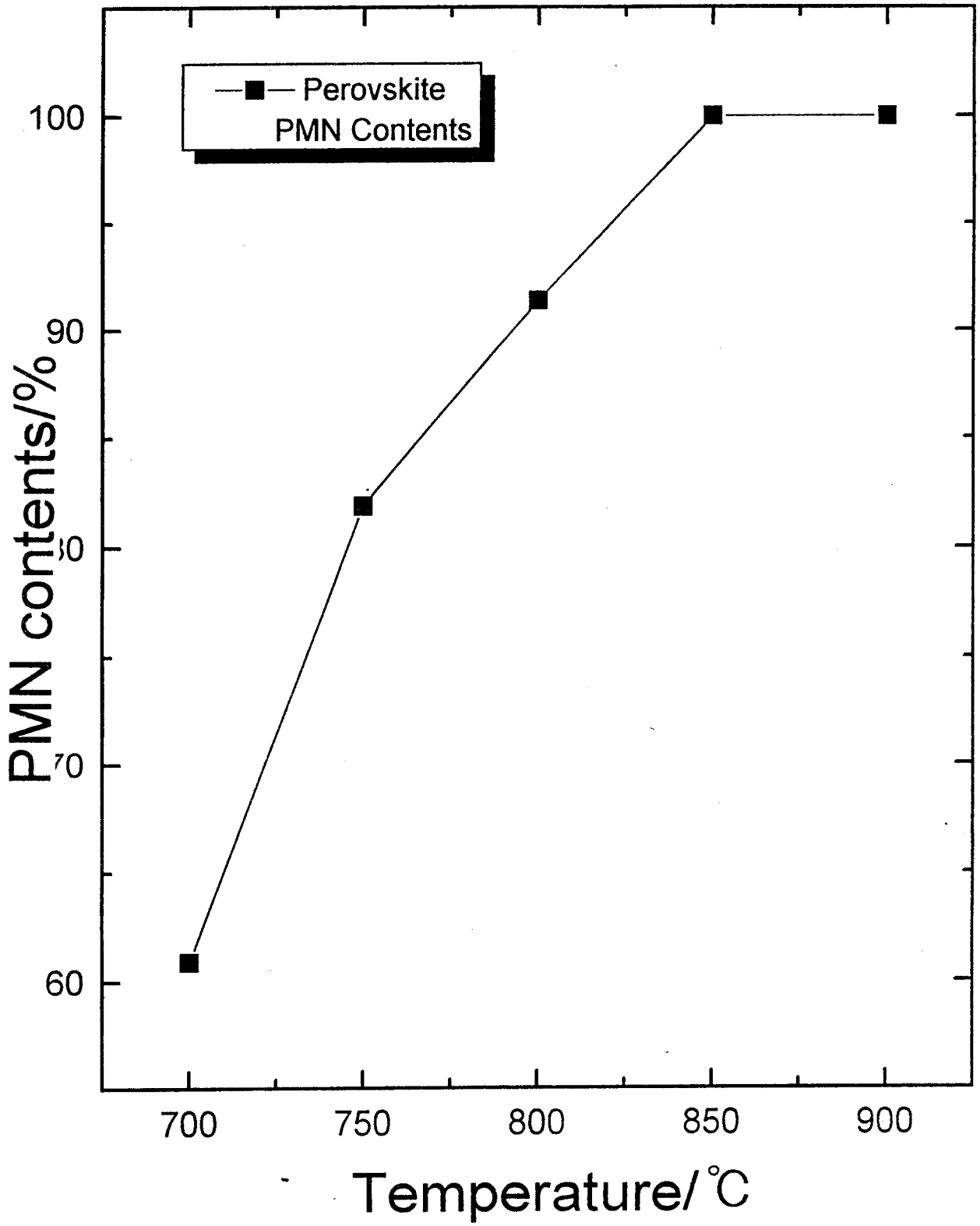


Fig. PMN contents of the powders with 10mol% excess MgO calcined at various temperatures.

결 론

○ $Nb(HC_2O_4)_5 \cdot nH_2O$, $Pb(NO_3)_2$, $Mg(NO_3) \cdot 6H_2O$를 출발물질로 선정하여 혼합수용액 제조

○ Kerosene, Span 80, Paraffin oil 을 이용한 유기상 제조

○ 혼합수용액의 에멀젼 제조

○ 800℃, 2시간 열처리로 100% PMN 합성