

# Microstructural Evolution and Dielectric Response Characteristics During Crystallization of Amorphous $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$

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Development of phases, evolution of microstructures, and dielectric response characteristics of amorphous lead iron tungstates during crystallization were investigated. A series of micrographs showing the evolution sequence of microstructures is presented. Crystallization was observed to initiate from inside of the amorphous material. A cubic perovskite phase developed fully at 760°C from amorphous state via intermediate metastable crystalline structures. Dielectric constant of amorphous PFW was totally insensitive to the temperature change around the Curie temperature of crystalline material. Sintered pellet, with relative density of 96% and an almost pore-free dense internal microstructure, could be prepared from amorphous powder.

**Key words :** Lead iron tungstate,  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ , Amorphous, Microstructural evolution, Crystallization.

## I. Introduction

Lead-based mixed B-site cation perovskite compounds, such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN), are promising candidates for electrical ceramic applications, including multilayer ceramic capacitors (MLCC's or chip capacitors), actuator elements, optical memory devices, etc. Among these, MLCC's with high specific capacitance, small temperature- and electric field-dependences, low sintering temperature, and low manufacturing cost have grown greatly in response to the development of surface mounting technology for miniaturization of electronic equipments. The low-temperature sinterability enables the use of a silver-rich Ag-Pd alloy as the internal electrode for the reduction of manufacturing cost.

Lead iron tungstate,  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW), is a typical relaxor ferroelectric material with a cubic perovskite structure,<sup>1,4)</sup> and was first synthesized in the late 1950's.<sup>5)</sup> PFW, in solid solution with PFN and/or other lead-based relaxor compositions, has been investigated primarily as potential materials for chip capacitors by the electronic component industry since mid-70's.<sup>3,6)</sup> Their main advantages over conventional  $\text{BaTiO}_3$  include low-temperature sinterability, high dielectric constant with diffuse character, and high voltage stability,<sup>7,8)</sup> which allow cost competitiveness, small size, and high reliability of the components. In PFW, the  $\text{Fe}^{3+}$  and  $\text{W}^{6+}$  ions were reported to be distributed randomly in the octahedral sublattice of the perovskite structure.<sup>9,10)</sup>

To date, however, most of the bulk specimens were prepared from the crystalline raw materials and relatively

little is reported on the preparation of amorphous powders from the so-called non-glass-forming materials, including PFW. Preparation of such materials into an amorphous state, in general, requires very high quenching rates to avoid rapid crystallization tendency during cooling. Knowledge of the structural development during crystallization may shed new insights into the microstructure control of ceramic bodies processed from amorphous materials. In this regard the crystallization behavior of amorphous PFW was studied, using differential thermal analysis (DTA), x-ray diffractometry (XRD), scanning electron microscopy (SEM), and dielectric spectroscopy. A possibility of using amorphous precursors for the preparation of densified ceramic dielectrics was demonstrated.

## II. Experimental

Amorphous lead iron tungstate was prepared in the form of thin flakes by rapid solidification from the melt of pre-synthesized perovskite powders. An extremely high quenching rate of  $\sim 10^6$  K/s was accomplished in the preparation by a twin-roller quencher, details of which were reported elsewhere.<sup>11)</sup> As-quenched flakes were examined using DTA at a heating rate of 10°C/min to study the thermochemical behavior. The flakes were then heat treated at several temperatures for 1 h, crushed into powders, and were examined using XRD (CuK $\alpha$ , Ni filter; 40 kV, 10 mA) to identify the phases developed. To obtain lattice parameters, a Nelson-Riley interpolation method was adopted for data refinement of XRD spectra.

Fractured and free surfaces of the as-quenched and heat-treated flakes were examined using SEM to study the evolution of microstructure. In the preparation of SEM specimen with a fractured surface, flakes (mounted on the specimen stage) were broken into several pieces with a slight pressure before the applied conducting adhesive was dried and were coated by gold sputtering.

Dielectric response of the flakes was also investigated over a temperature range of  $-150^{\circ}$  to  $500^{\circ}\text{C}$ , to study the properties of PFW in the amorphous state and during crystallization. For dielectric measurements, silver electrodes were applied on both sides of the flakes followed by curing at  $600^{\circ}\text{C}$ . The measurements were carried out on heating using a temperature control unit and an impedance analyzer (HP4192A) at  $10^3$  to  $10^6$  Hz under an oscillation field of  $1.0 \text{ V}_{\text{rms}}/\text{mm}$ .

To demonstrate the possibility of preparing dense ceramic bodies from amorphous precursor materials, the flakes were ground into fine powders, uniaxially pressed at  $100 \text{ MPa}$  into pellets, and were fired. Apparent density of the sintered pellet was determined by a water displacement method. Finally, microstructures of the sintered pellets were examined.

### III. Results and Discussion

A DTA thermogram of the as-quenched flakes is illustrated in Fig. 1, where a glass transition endotherm starting at  $350^{\circ}\text{C}$ , two crystallization exotherms at  $395^{\circ}$  and  $475^{\circ}\text{C}$ , two additional endotherms at  $680^{\circ}$  and  $730^{\circ}\text{C}$ , and a final endotherm of melting at  $935^{\circ}\text{C}$  are shown. Based on the thermal events,  $380^{\circ}$ ,  $400^{\circ}$ ,  $510^{\circ}$ ,  $690^{\circ}$ , and  $760^{\circ}\text{C}$  were selected as temperatures of heat treatment.

Phases developed after the heat treatment were analyzed by powder XRD, and the spectra are shown in Fig. 2. Diffraction pattern of the as-quenched flakes is also included, which showed only a broad diffuse scattering, characteristic of an amorphous state. In contrast, as-quenched flakes of PZN-BZN system (using similar apparatus)

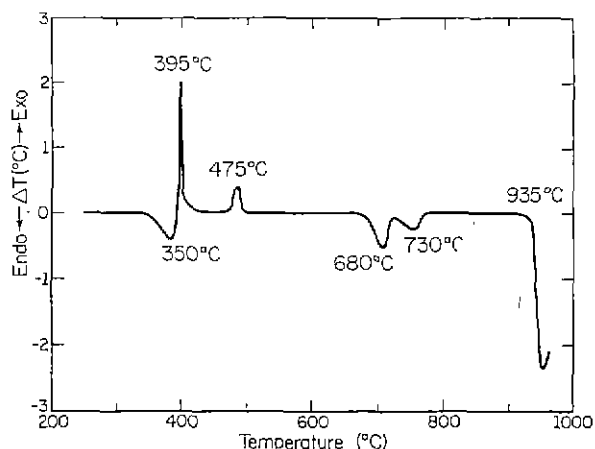


Fig. 1. DTA thermogram of as-quenched flakes, showing thermochemical events.

was reported to be crystalline,<sup>12)</sup> due to their low quenching rate (rotating speed of  $50\sim 100 \text{ rpm}$  vs.  $3,000 \text{ rpm}$ <sup>11)</sup>) and a consequent thicker dimension ( $30\sim 200 \mu\text{m}$  vs  $15\sim 25 \mu\text{m}$ <sup>11)</sup>) of flakes, leading to slower rate of heat dissipation during quenching. After a heat treatment of amorphous PFW flakes at  $380^{\circ}\text{C}$ , similar pattern (to the as-quenched PFW) without any development of diffraction peaks was observed, so was not included in Fig. 2. After a  $400^{\circ}\text{C}$ -treatment, however, several peaks started to appear, indicating the initiation of crystallization. Heat treatment at  $510^{\circ}$  and  $690^{\circ}\text{C}$  resulted in similar patterns (but different from that of  $400^{\circ}\text{C}$ -treatment). Considering the location of the peaks, these  $510^{\circ}$  and  $690^{\circ}\text{C}$  patterns seem to be associated with the pyrochlore structure, but could not be matched with any of JCPDS files for the  $\text{PbO-Fe}_2\text{O}_3\text{-WO}_3$  system.

A cubic form of perovskite structure (JCPDS 15-554) started to develop from  $510^{\circ}\text{C}$  and reached the highest content after a  $760^{\circ}\text{C}$ -treatment at the expense of the intermediate phases, with a minor amount of  $\text{Pb}_2\text{WO}_5$  (JCPDS 24-591). The absence of superstructural lines in the perovskite pattern confirms that the  $\text{Fe}^{3+}$  and  $\text{W}^{6+}$  ions are disorderly distributed in the B-site. The lattice parameter of the fully developed cubic perovskite phase was calculated to be  $3.983 \text{ \AA}$ , which is in good agreement with the reported data.<sup>14)</sup> During the crystallization process, the flakes turned to opaque grayish-black color from transparent reddish-brown of the as-prepared

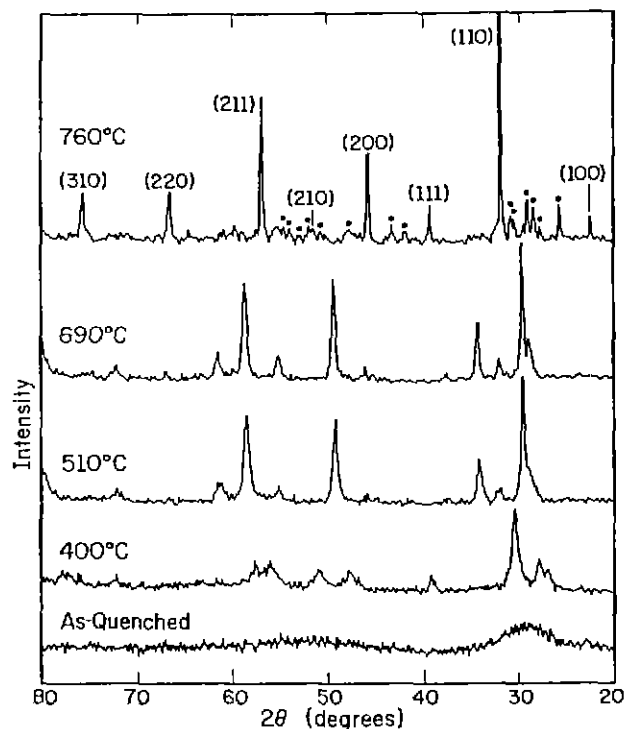


Fig. 2. X-ray diffraction spectra of as-quenched and heat-treated flakes. Diffraction peaks associated with the perovskite phase are indexed, while those for  $\text{Pb}_2\text{WO}_5$  are marked with solid dots.

state.

In the crystallization process of rapidly solidified material, in general, one or more intermediate metastable crystalline phase(s) form initially from the amorphous state, followed by subsequent conversion to more stable phase(s) at elevated temperatures.<sup>13,14</sup> Amorphous PFW followed a similar trend on crystallization; i.e., the cubic perovskite phase crystallized via intermediate phases, as revealed in Fig. 2. The intermediate phases may also be metastable and may not be accessible in any other way.

In Fig. 3 is a fracture area of the as-quenched flake, where a fracture mode of a conchoidal nature - characteristic of a glassy material - can clearly be observed. The conchoidal fracture mode confirms the amorphous

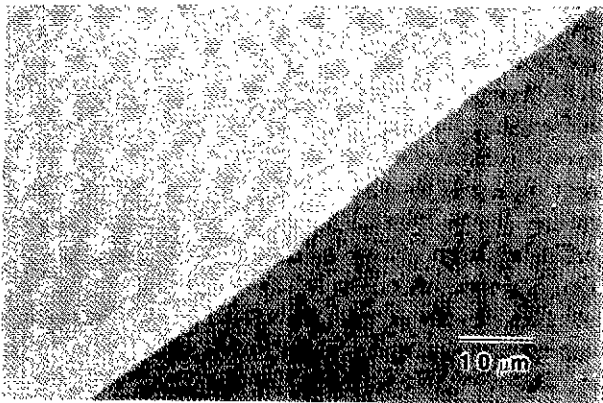


Fig. 3. Fracture region of an as-quenched flake, showing a conchoidal fracture mode.

structure of the quenched flakes, which was also verified from the X-ray pattern. Fig. 4 is a micrograph showing a cracked region after a heat treatment at 400°C, which reveals that crystallization had initiated from inside of the flakes. The initiation of crystallization at 400°C was also observed in Fig. 2. A series of micrographs, illustrating the structure evolution sequences from internal crystallites during a heat treatment at 690°C, is presented in Fig. 5. The micrographs illustrate several intermediate stages of development, where internally-nucleated crystallites (e.g., Fig. 4) (A) grow towards the surface and lead to surface swelling, (B and C) disrupt the surface, and (D) finally form a crystal of  $\approx 5 \mu\text{m}$  in size.

Next two micrographs are obtained from partially and



Fig. 4. A cracked region after a 400°C heat-treatment, revealing an internally grown crystal.

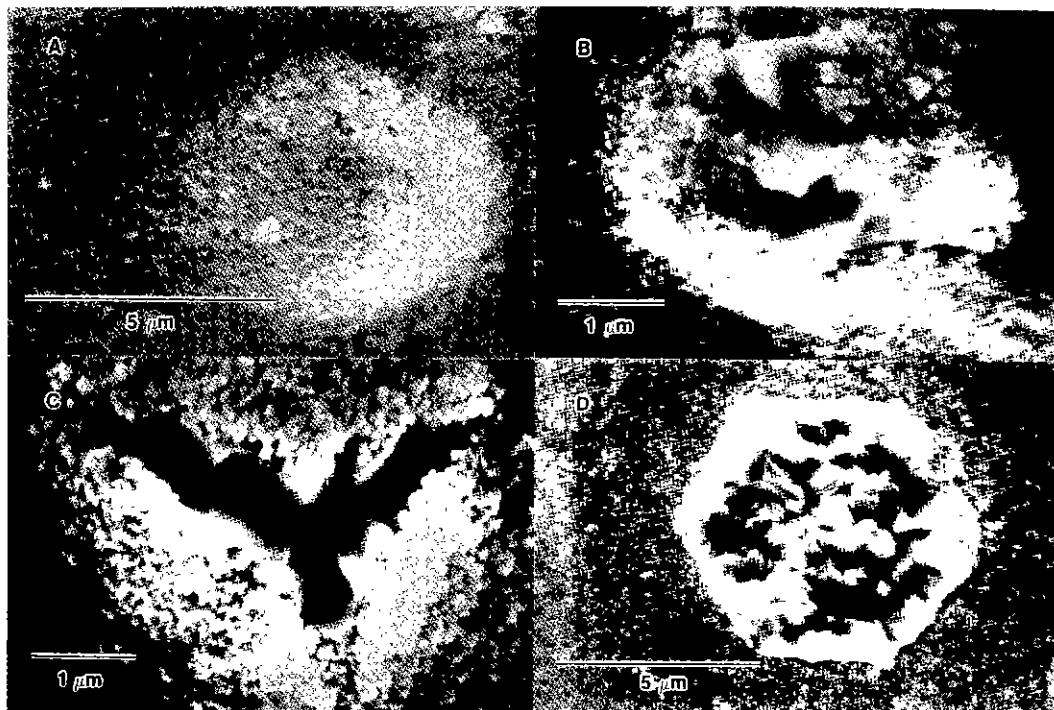


Fig. 5. A sequence of microstructure development from an internal crystallite, after a heat-treatment at 690°C. Refer to text for details.

fully crystallized regions of flakes heat-treated at 760°C. Fig. 6 shows a region, where aggregates of cuboid crystals, developed from the matrix of flakes, can be observed. Development of crystals could be noticed along the border region between the cluster of crystals and the matrix. Large degree of crack development in the matrix arises from the shrinkage of free volume (of amorphous flakes) during the crystallization process. A wide area of fully developed cuboid crystals is presented in Fig. 7. Such grain cuboidization was also reported on MgO-MgCl<sub>2</sub> system during sintering,<sup>15</sup> sol-gel-derived PFW,<sup>16</sup> and heat-treated PZN/PbO,<sup>17</sup> but the degree of uniformity in size and shape (regular cuboid form) is more pronounced in the case of PFW.

An amorphous phase usually has a lower dielectric constant than the corresponding crystalline form due to the presence of free volume in the glassy state. This is the case for amorphous PFW, too. Fig. 8 illustrates the temperature dependence of dielectric constant for amorphous PFW during crystallization as a function of frequency. A 10 kHz dielectric spectrum for polycrystalline PFW, taken from a literature,<sup>10</sup> is also included in the figure for comparison. Crystalline PFW shows a diffuse phase transition (resulting from compositional heterogeneities by random distribution of competing iron



Fig. 6. Development of cubic perovskite crystallites at 760°C.

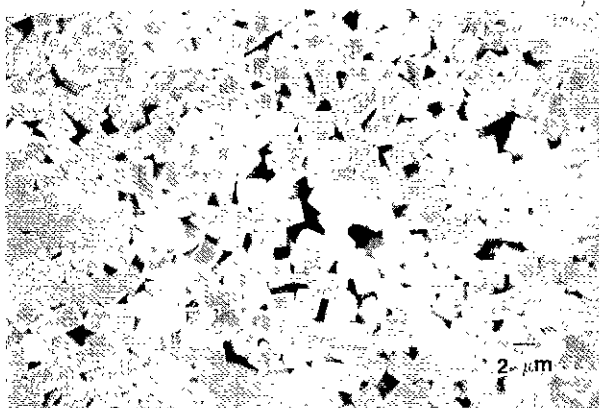


Fig. 7. Uniform microstructure of cuboid surface crystals, fully developed after a heat-treatment at 760°C.

and tungsten ions for the B-site sublattice in the perovskite structure) around -95°C for the paraelectric-ferroelectric phase transition.<sup>2,10</sup> Meanwhile dielectric constant spectrum for amorphous PFW did not show any corresponding peak, since there is not any phase transformations in the amorphous materials. Dielectric constant of amorphous PFW around -95°C was significantly lower than the value of crystalline material due to the lack of ferroelectric coupling. In the crystalline state, the ferroelectrically active BO<sub>6</sub> octahedra are coupled to each other via the A-site cations of Pb<sup>2+</sup>, and as a result high values of dielectric constant arise.

The dielectric constant of amorphous PFW at room temperature was about 44 over the whole frequency range, which is rather high for an amorphous material. This high value is ascribed to the possible retention of short-range order in the nearest neighbor configuration of oxygen octahedron cages around the Fe<sup>3+</sup>/W<sup>6+</sup> ions as well as associated ionic polarizability. Amorphous PLZT prepared by sol-gel processing<sup>18</sup> also showed a high dielectric constant of ~40 with similar reasoning. The apparent dielectric constant increased with increasing temperature above 200°C. Fig. 8 shows a trough at 350°C (marked with an arrow; associated with the glass transition) and two inflections in the curve at 380° and 480°C (also marked with arrows; associated with crystallization phenomena). The anomalous increase in dielectric constant at elevated temperatures was reported to be associated with enhanced conductivity (transport polarization rather than displacement polarization).<sup>6,19</sup> The tendency in the frequency dispersion of dielectric constant increased with temperature.

To obtain dense ceramic bodies, pressed pellets were fired at 880°C for 2 h. Sintering at a rather low temperature was possible due to the low melting tem-

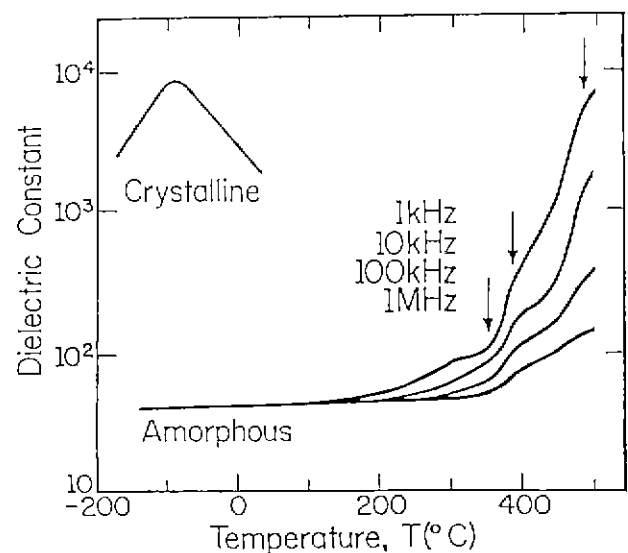


Fig. 8. Temperature and frequency dependence of dielectric constant for amorphous PFW. For crystalline data, see Ref. 10.

perature of 935°C (Fig. 1). Actually PFW has the lowest melting point among the lead-based relaxor compounds with high maximum dielectric constants. The x-ray spectrum of the sintered body was similar to that of 760°C heat treatment (top pattern of Fig. 2). Apparent density of the pellet was measured to be 8.90 g/cm<sup>3</sup> (96% of theoretical). Fig. 9 shows (A) fractured and (B) free surfaces of the sintered pellet, where an almost pore-free internal microstructure (composed of deformed cubes) with intergranular fracture mode could be observed. In contrast, the free surface showed a similar microstructure as Fig. 7, but with rounded corners of cuboid crystals ranging 1-2 μm. Thus, the possibility of using amorphous precursors in the processing of dense ceramic bodies was demonstrated.

#### IV. Summary

A cubic phase ( $a=3.983$  Å) of PFW in the complex perovskite structure, with a random distribution of Fe<sup>3+</sup> and W<sup>6+</sup> ions in the B-site, developed from amorphous state via intermediate metastable phases with heat treatments. The intermediate phases were developed from the amorphous flakes after heat treatments up to 690°C. As-quenched flakes showed conchoidal fracture mode and confirmed the amorphous nature, also revealed by X-ray pattern. Bulk nucleation was verified by SEM ob-

servation of the 400°C heat treated flake. A very uniform microstructure of cubic perovskite crystals ( $\approx 2$  μm) was obtained after a heat treatment at 760°C. Dielectric spectra of amorphous PFW did not show any peaks around the crystalline Curie temperature of -95°C. Room temperature dielectric constant was  $\approx 44$ , which is a rather high value for an amorphous material. Apparent density of the sintered ceramic body was 96% of a theoretical value, thus possibility of using amorphous precursors in the preparation of densified ceramic dielectrics was demonstrated.

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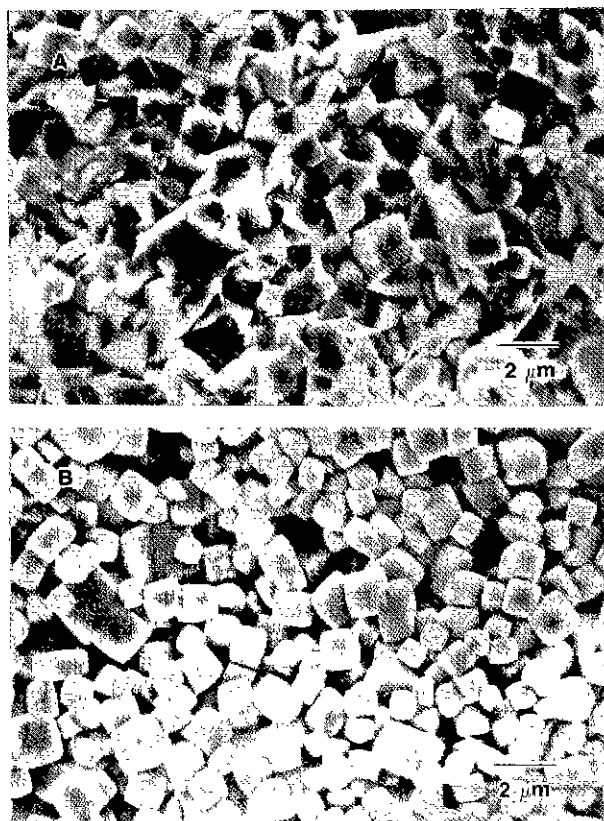


Fig. 9. (A) Fractured and (B) free surfaces of a sintered pellet, showing a dense microstructure.

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