Rapid Quenching and Dielectric Properties of $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$

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超急冷法によって作製した $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ の誘電的性質

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The dielectric properties of amorphous $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMW) prepared by a rapid quenching method were investigated. A dielectric anomaly was found at 650 K. This can be explained by its glass transition and crystallization process. The dielectric properties of annealed PMW was also investigated. A dielectric peak was observed at 283 K. This can be attributed to a phase transition in the precipitated perovskite phase, though the transition temperature was 30 K below that of sintered PMW.

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1. Introduction

A roller quenching method has been used to prepare many amorphous oxides for exploring new functional ceramics. Amorphous states of ferroelectric materials, such as LiNbO_3 ¹⁾ and PbTiO_3 ,²⁾ prepared by roller quenching has been studied because of the possibility of preparing high dielectric constant materials based on a model first proposed by Lines.³⁾ In addition, the appearance of metastable phases has been frequently observed by heat treatments of amorphous oxides.⁴⁾ Their electrical properties also offer considerable interest.

This paper describes the dielectric properties of amorphous $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMW) prepared by a roller quenching method. PMW is an antiferroelectric material below the phase transition at 314 K.⁵⁾ PMW has a perovskite type structure with its B-site cations, Mg^{2+} and W^{6+} , being ordered.⁶⁾ Drastic changes of dielectric properties are discussed in relation to its crystal structure change due to quenching and subsequent heat treatments.

2. Experimental

Samples were prepared from stoichiometric proportions of PbO , MgO , and WO_3 by firing at 1073 K for 4 h. After pressing into pellets, samples were sintered at 1173 K for 2 h. A twin-roller apparatus was used to produce rapidly quenched samples. After the sintered pellets being melted, the melts were squirted out of the Pt crucible with

a pressure of argon and injected between rotating steel rollers. Quenched flakes were reground, and pressed into pellets. Some of these pellets were reheated at various temperatures between 673 and 1173 K for 1 h to prepare annealed samples.

The crystal structure was examined using X-ray powder diffraction measurements (XRD) with $\text{CuK}\alpha$ radiation. Thermal properties were investigated using a differential scanning calorimeter (DSC) with a scanning rate of 20 Kmin^{-1} .

For dielectric measurements, pellets were polished and Pt-Pd electrodes were sputtered. Dielectric properties as a function of temperature (173 to 873 K) and frequency (1 kHz and 10 kHz) were measured with a three-electrode method in a field of 50 Vcm^{-1} using a YHP model 4274A LCR meter.

3. Results

3.1 Formation of an amorphous state

Roller-quenched flakes were yellowish and glossy. An XRD pattern of ground flakes quenched under an optimum condition evidently shows the formation of an amorphous state (Fig. 1(b)). A few diffraction lines of crystalline Pb_2WO_5 are observed even in this XRD pattern, indicating that it contained somewhat crystalline regions. It should be noted here that preparation of a uniform sample using a roller quenching method is very difficult.

Decreases in applied Ar pressure and rotational

Fig. 1. X-ray diffraction patterns of (a) sintered PMW and (b) quenched PMW.

speed of rollers resulted in an increase in Pb_2WO_5 content because of a decrease in a quenching rate. The amount of Pb_2WO_5 decreased with elevating temperature of the melt before quenching. But above 1400K, intense volatilization of PbO from the melt was observed. This might shift the chemical composition of the quenched PMW. Thus an optimum quenching condition was determined as follows: (1) Temperature of the melt before quenching is 1400K, (2) an applied Ar pressure is 0.2MPa, (3) rotational speed of rollers is 5000rpm. Chemical analysis data for PMW quenched under this condition were in good agreement with the calculated values. In the following sections, results are described for the samples prepared under this condition.

3.2 Crystallization

Formation of an amorphous state in quenched PMW was confirmed by DSC measurements. A typical DSC curve is shown in Fig. 2(b). Two exothermic peaks observed at 675 and 700K are ascribed to crystallization of the amorphous phase. They are preceded by a slight change of a baseline at 645K caused by a glass transition. Note that there are no peak near 314K, at which temperature an orthorhombic-cubic phase transi-

Fig. 2. Typical DSC curves of (a) sintered PMW and (b) quenched PMW.

Fig. 3. X-ray diffraction pattern of PMW annealed at 873K for 1h.

Fig. 4. Effect of annealing temperature on the crystalline phases appeared.

tion occurs and a sharp endothermic peak is observed for sintered PMW (Fig. 2(a)).

Crystalline phases which appeared when quenched PMW was heated above the crystallization temperature were next examined. In a sample annealed at 873K for 1h, three phases were identified from XRD analysis: (A) perovskite type $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$, (B) scheelite type PbWO_4 , and (C) orthorhombic Pb_2WO_5 (Fig. 3). Contents of the above three phases in samples annealed at various temperatures were estimated from the intensity of the strongest XRD peak of each phase (Fig. 4). PbWO_4 and Pb_2WO_5 , passing through the maximum at 873K, decreased to a small value with the elevation of annealing temperature. In contrast, $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ monotonously increased with the elevation of annealing temperature. Even at the highest annealing temperature of 1173K, however, the single perovskite phase was not achieved for annealed PMW.

Fig. 5. Temperature dependence of the dielectric constants for quenched PMW.

Fig. 6. Temperature dependence of the dielectric losses for quenched PMW.

Fig. 7. Temperature dependence of the dielectric constants for annealed PMW.

3.3 Dielectric properties

Temperature dependence of the dielectric constants for quenched PMW showed a diffuse peak near 650 K (Fig. 5). Below that, no anomalous behavior was observed. The steep rise of the dielectric constants above 700 K is attributed to increasing ionic conductivity, since it was accompanied with frequency dispersion and a dielectric loss increase (Fig. 6).

Crystallization might cause considerable changes in the dielectric properties. Figure 7 shows the temperature dependence of the dielectric constants in the temperature range between 173 and 373 K for PMW annealed at 1173 K for 1 h. No anomalous dielectric behavior was detected above 373 K. The pronounced dielectric peak is observed at 283 K. This peak can be attributed to a phase transition in the perovskite phase precipitated in annealed PMW, since no such anomaly is considered to exist in PbWO_4 and Pb_2WO_6 near this temperature. But the transition temperature was 30 K below that of sintered PMW.

4. Discussion

4.1 Dielectric properties of quenched PMW

Dielectric measurements have been done for an amorphous state of ferroelectric materials such as LiNbO_3 and PbTiO_3 . Glass et al.¹⁾ reported that amorphous LiNbO_3 showed a dielectric anomaly 150 K below the crystallization temperature. They suggested that it was a ferroelectric transition. But amorphous PbTiO_3 and LiNbO_3 -BaO measured by Takashige et al.²⁾ and Tatsumisago et al.,⁷⁾ respectively, showed no evidence of ferroelectric transitions.

The dielectric constants of quenched PMW showed one peak near 650 K (Fig. 5). This temperature is between its glass transition and crystallization temperature measured by DSC (Fig. 2). Furthermore the dielectric losses showed a peak at the same temperature (Fig. 6). Hence the dielectric behavior near 650 K can be explained by an increase of ionic conductivity due to the relaxation of a frozen ionic motion, followed by a decrease of ionic conductivity due to crystallization. Since no anomaly was observed between 173 and 650 K, quenched PMW is considered to be paraelectric above 173 K.

4.2 Dielectric properties of annealed PMW

The dielectric constants of annealed PMW showed a pronounced peak at 283 K (Fig. 7), which could be attributed to a phase transition of the precipitated perovskite phase. Evidence of a phase transition was obtained from DSC measurements with an endothermic peak on heating and its reversibility (Fig. 8). This transition was

Fig. 8. DSC curves of the phase transitions in (a) sintered PMW and (b) annealed PMW.

characterized by a lower transition temperature and broadening of the peak compared with that of sintered PMW. The possible explanations for them are as follows: (1) a change in the chemical composition for an entire sample caused by volatilization of PbO from the melt, (2) a change in the chemical composition for the perovskite phase caused by co-precipitations of PbWO_4 and Pb_2WO_5 , (3) a structural change in the perovskite phase (the ordering of Mg^{2+} and W^{6+}), (4) distortions in the perovskite structure.

Since chemical analysis data of quenched PMW were in good agreement with the calculated values, the first explanation can be ruled out. Regarding to the third one, XRD data evidently showed the superlattice line at $2\theta \sim 19^\circ$, indicating the ordering of Mg^{2+} and W^{6+} (Fig. 3). The intensity ratio of the superlattice line to the strongest diffraction line for annealed PMW was almost equal to that for sintered PMW. Thus the precipitated perovskite phase is identical with a

sintered one in terms of ordering of Mg^{2+} and W^{6+} .

The most reasonable explanation is the second one: Precipitations of stable PbWO_4 and Pb_2WO_5 results in the excess MgO in the perovskite phase, and replacement of Pb^{2+} by Mg^{2+} would be expected to lower the transition temperature. In this study, however, the data for the stoichiometry and distortions in the precipitated perovskite phase could not be obtained. Further analyses of the microstructure and the composition are desired.

5. Summary

The results of this investigation were: (1) Amorphous PMW was obtained by a rapid quenching method using a twin-roller apparatus. (2) The dielectric constants of quenched PMW showed a peak at 650 K. This could be explained by ionic conductivity change due to its glass transition and crystallization process. (3) Three crystalline phases ($\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$, PbWO_4 , Pb_2WO_5) were found when the quenched PMW was heated above the crystallization temperature. (4) The dielectric constants of annealed PMW showed a peak at 283 K. This was attributed to a phase transition in the precipitated perovskite phase, though the transition temperature was 30 K below that of sintered PMW.

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