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Preparation and thermal decomposition of new pyrochlore $Pb_2FeWO_{6.5}$

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A new compound $Pb_2FeWO_{6.5}$ having a pyrochlore structure has been synthesized by soaking the powder prepared from coprecipitation at 650 °C for 30 d. Using a conventional solid-state reaction, single-phase $Pb_2FeWO_{6.5}$, however, cannot easily be obtained. The coprecipitation technique not only contributes to the completion of reactions, but also lowers the formation temperatures. Enhanced homogeneity and reactivity in coprecipitated powder are considered to accelerate the progress of the reactions. $Pb_2FeWO_{6.5}$ is determined to be characteristic of a cubic pyrochlore structure having a lattice parameter $a_0 = 1.0432$ nm. This compound exists stably below 700 °C, above which it decomposes to $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$. A drastic change in microstructure is induced after complete decomposition at 860 °C.

1. Introduction

Pyrochlore compounds have been known as intermediates usually existing in the formation process of a greater part of the lead-containing complex oxides [1]. Most of them form only in reaction sequences and convert to perovskite phases after the completion of the reactions. But in certain systems, such as $PbZn_{1/3}Nb_{2/3}O_3$, $PbMg_{1/3}Nb_{2/3}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ [2, 3], the subsequent transformation of pyrochlore phase to perovskite phase proceeds very slowly, leading to the two phases coexisting stably. The remaining pyrochlore phases will have detrimental effects on dielectric properties of ferroelectric ceramics [4]; therefore, new synthesis methods have recently been developed to obtain pyrochlore-free compounds [5, 6]. Although this kind of research is possible, studies on the synthesis of pyrochlore phases have been few.

In the formation process of $PbFe_{2/3}W_{1/3}O_3$ from $3PbO–Fe_2O_3–WO_3$ mixture, a pyrochlore phase appears as a transient compound which converts to perovskite phase at elevated temperatures [1, 7, 8]. From the X-ray diffraction data of the pyrochlore–perovskite mixture, this pyrochlore is characterized by a cubic structure with $a_0 = 1.0442$ nm [9]. The composition of pyrochlore is assumed to be $Pb_2Fe_{2/3}W_{4/3}O_7$ with an atomic ratio of Pb:Fe:W = 3:1:2 by Agranovskaya [1]. However, the composition of the pyrochlore phase with a plate-like shape forming in a liquid-phase reaction of $3PbO–Fe_2O_3–WO_3$ was found to have an atomic ratio of Pb:Fe:W = 2:1:1 in a previous study [10]. Thus, there is a difference between Agranovskaya's report and our results. In order to clarify the confusion over the chemical composition of the pyrochlore phase, the synthesis of its pure compound is considered to be a direct approach.

In the present investigation, two methods of synthesis, i.e. solid-state reaction and coprecipitation, were used to prepare $Pb_2FeWO_{6.5}$. Thermal analysis and heat treatment for the prepared powder were carried out to investigate the optimum firing condition. The crystallographic data of synthesized $Pb_2FeWO_{6.5}$ are described and the thermal decomposition behaviour of $Pb_2FeWO_{6.5}$ is also discussed.

2. Experimental procedure

Starting materials corresponding to an atomic ratio of Pb:Fe:W = 2:1:1 were prepared by solid-state reaction and coprecipitation. In the former method, reagent grade PbO, Fe_2O_3, and WO_3 in molecular proportions $4PbO–Fe_2O_3–2WO_3$ were ball-milled for 2 d using a resin mill and resin balls with ethyl alcohol, and then dried.

In the coprecipitation method, raw materials of $Pb(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, and $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ were utilized to prepare solutions of each cation. The required amounts of lead and tungsten solutions were first blended together and white $PbWO_4$ precipitated immediately. Then iron solution and dilute ammonia were added to the above slurry and mixed using a magnetic stirrer. After ammonia precipitated all of the residual ions, a clear solution was formed. Through filtering and drying, the dried coprecipitate was obtained.

The dried powder was pulverized and pressed into compacts under 98 MPa, and fired at temperatures from 250 to 860 °C at 50 °C intervals for 2 h soaking per interval. The regulation of soaking time and the

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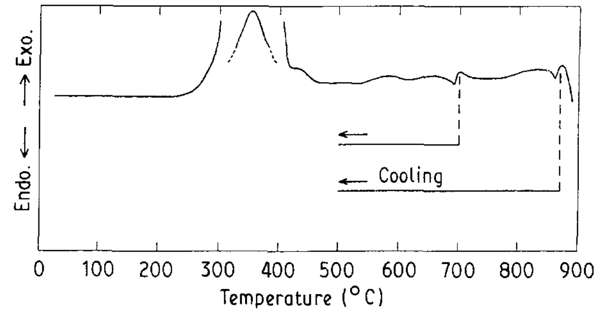

Figure 1 Differential thermal analysis of 4PbO–Fe_2O_3–$2WO_3$ powder.

repetitive treatment of grinding and firing were also carried out. Fluorescent X-ray analysis was used to examine the compositions of fired samples. Powder X-ray diffraction analysis (XRD) was performed to identify the resulting phases. Slow scanning at 0.12° $2\theta\ \mathrm{min}^{-1}$ was used to obtain accurate diffraction data. Lattice parameters were calculated from the data corrected by internal silicon standard (NBS no. 640) through the least square method. Differential thermal analysis (DTA) and thermogravimetry (TG) were conducted at a rate of $5\,^{\circ}\mathrm{C\,min}^{-1}$. Scanning electron microscopy (SEM) was used to observe the microstructure of specimens.

3. Results

3.1. Thermal analysis and XRD study of the solid-state reaction

Fig. 1 shows the DTA curve of the mixed oxides of 4PbO–Fe_2O_3–$2WO_3$ prepared through the solid-state reaction. The large exothermic peak occurring from 300 to 400 °C was due to the combustion of a resin contaminant from the ball-milling. In addition to this peak, two small endothermic peaks appeared at around 690 and 860 °C. The curve of DTA fell down rapidly to an endothermic direction from the base line after the 860 °C peak, indicating that melting occurred. Two cooling runs were conducted after the endothermic peaks appeared at 690 and 860 °C, but no DTA peaks were detected during the cooling run. A large amount of pyrochlore phase with residual compounds ($PbWO_4$, Pb_2WO_5, and Fe_2O_3) were found in the sample cooled after the 690 °C peak. However, only $PbWO_4$ and $PbFe_{2/3}W_{1/3}O_3$ existed after the 860 °C peak.

The results of XRD for the 4PbO–Fe_2O_3–$2WO_3$ mixture fired for 2 h at each soaking temperature from 250 to 860 °C are shown in Fig. 2. During the heating treatment, lead tungstates, i.e. $PbWO_4$ and Pb_2WO_5, appeared as the first two products and increased with a corresponding decrease of reactants PbO and WO_3. $PbWO_4$ was observed above 300 °C and decreased to 700 °C after reaching its maximum at about 400 °C. Pb_2WO_5 formed at around 350 °C and increased in amount as $PbWO_4$ decreased. The reaction of Fe_2O_3 with other compounds was slow and its amount was reduced gradually to 700 °C, which indicated the poor reactivity of Fe_2O_3. An unidentified phase, presumably an iron-containing compound, appeared at around 500 °C. The pyrochlore phase began to form at 600 °C and reached its maximum amount at 700 °C with other residual phases. Above 700 °C, the pyrochlore phase was reduced and the formation of $PbWO_4$ and $PbFe_{2/3}W_{1/3}O_3$ apparently increased. All of the pyrochlore phase had disappeared at 860 °C and only $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ remained. These XRD results of the fired samples were in agreement with those of cooled samples in from the DTA runs.

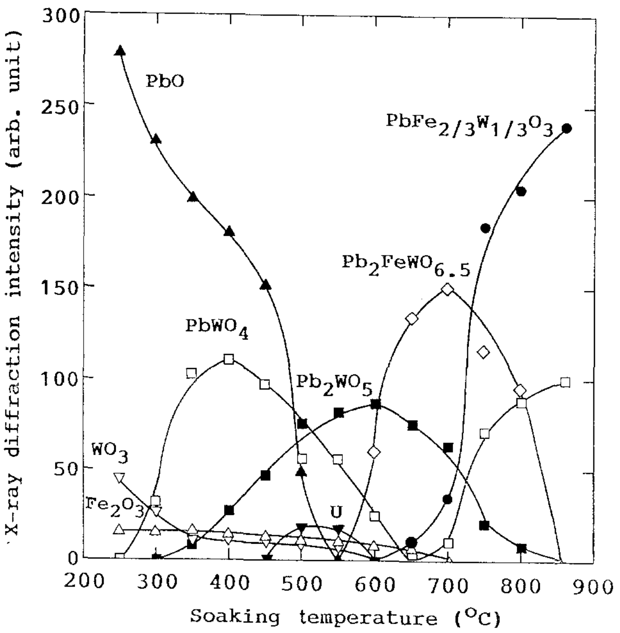

Figure 2 X-ray diffraction intensity of the resulting compounds plotted against soaking temperature for 4PbO–Fe_2O_3–$2WO_3$ powder. (▲) PbO, (△) Fe_2O_3, (▽) WO_3, (□) $PbWO_4$, (■) Pb_2WO_5, (▼) unidentified, (◇) $Pb_2FeWO_{6.5}$, (●) $PbFe_{2/3}W_{1/3}O_3$.

Because the amount of pyrochlore phase was increased at 600 to 700 °C, it was attempted to produce a pure pyrochlore phase through soaking samples in the above temperature range. Although repeated firing and grinding treatments were carried out and the soaking time was prolonged to 30 d, a pure pyrochlore phase could not be obtained. Thus a pure pyrochlore phase is obviously difficult to synthesize by solid-state reaction.

3.2. Thermal analysis and XRD study for coprecipitation

Fig. 3 shows the TG–DTA curves of the mixture obtained from coprecipitation. A weight loss of about 7% occurred when the sample was heated up to 400 °C, in the TG curve. Compared with the results of DTA, the weight loss was thought to be due to the evolution of absorbed H_2O and NH_4OH in the samples, which also formed two exothermic reactions at 100 and 400 °C in DTA. A large exothermic peak observed at 300 °C resulted from the crystallization of $PbWO_4$. The DTA curve returned to its base line above 500 °C at which the pyrochlore began to appear. Above that, there were no distinct changes, except for an endothermic peak at 855 °C. Subsequently, the DTA curve fell in an endothermic direction similar to Fig. 1. When cooling was conducted in

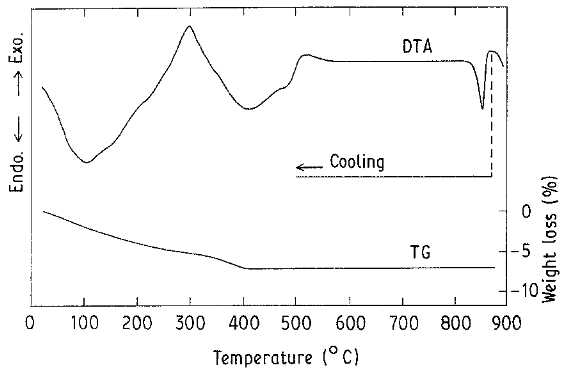

Figure 3 Thermogravimetric and differential thermal analysis of the coprecipitated powder having an atomic ratio of Pb:Fe:W = 2:1:1.

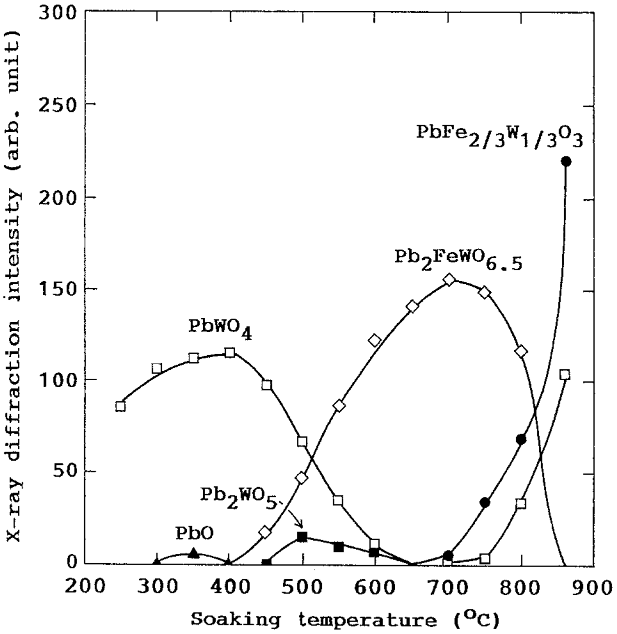

Figure 4 X-ray diffraction intensity of resulting compounds plotted against soaking temperature for the coprecipitated powder having an atomic ratio of Pb:Fe:W = 2:1:1. (▲) PbO, (□) $PbWO_4$, (■) Pb_2WO_5, (◇) $Pb_2FeWO_{6.5}$, (●) $PbFe_{2/3}W_{1/3}O_3$.

DTA after the end of the 855 °C peak, no DTA peak was detected and the cooled sample was found to consist only of $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$. When the sample was cooled at 830 °C lower than the 860 °C endothermic peak, a large amount of pyrochlore phase was observed with $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$.

The resultant phases of fired precipitates formed as a function of soaking temperature are shown in Fig. 4. When heated up to 400 °C, a large amount of $PbWO_4$ and traces of PbO were formed. Pyrochlore first appeared at 450 °C and then correlatively increased with the decrease of $PbWO_4$ up to 700 °C. A small amount of Pb_2WO_5 was also detected between 500 and 600 °C. A single pyrochlore phase was obtained at around 650 °C. Higher than 700 °C, the pyrochlore phase gradually decomposed to $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$. When heating at 860 °C, only $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ coexisted without the pyrochlore phase.

A pure pyrochlore phase was obtained when soaking at 650 °C for 2 h; however, the X-ray diffraction peaks were somewhat broader. A prolonged soaking process was found to be effective in reducing the half-widths of diffraction peaks, implying that the crystallinity of the compound was improved. The change in half-widths and intensities of the (4 0 0), (4 4 0), and (6 2 2) diffraction peaks with soaking time is indicated in Fig. 5. Through 30 d soaking at 650 °C, a pure pyrochlore phase, having a sharp X-ray diffraction pattern, was produced.

The chemical composition of the pyrochlore phase was analysed by fluorescent X-ray analysis and found to be in good agreement with the composition of the starting materials having an atomic ratio of Pb:Fe:W equal to 2:1:1. The oxygen content was calculated from the residual weight fraction, and the resultant composition of the pyrochlore phase was concluded to be $Pb_2FeWO_{6.5}$.

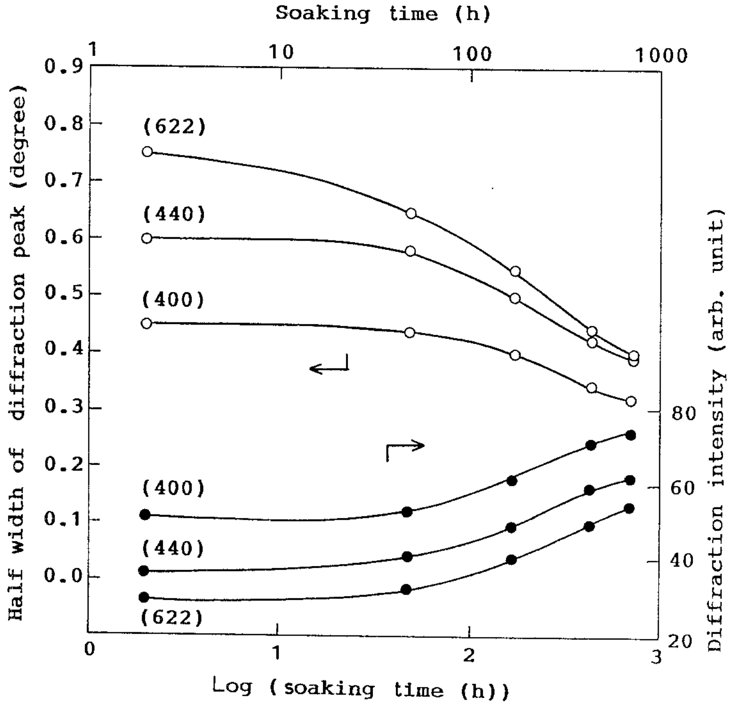

Figure 5 Half-width and intensity of (4 0 0), (4 4 0), and (6 2 2) X-ray diffraction peaks plotted against soaking time for $Pb_2FeWO_{6.5}$ soaked at 650 °C.

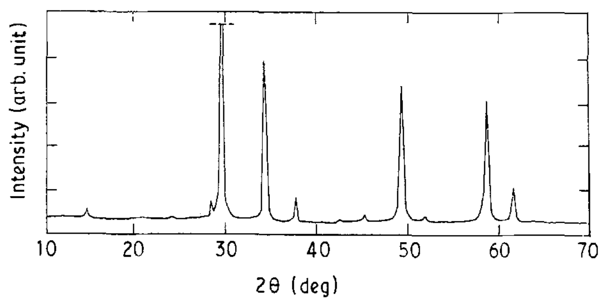

Figure 6 X-ray diffraction pattern of $Pb_2FeWO_{6.5}$ soaked at 650 °C for 30 d.

$Pb_2FeWO_{6.5}$ is essentially isostructural with the pyrochlore-type having a general formula $A_2B_2O_7$. Its resultant X-ray diffraction pattern is shown in Fig. 6 and the X-ray diffraction data are presented in Table I. Based on these results, $Pb_2FeWO_{6.5}$ was determined to be characteristic of a cubic pyrochlore structure having a lattice parameter $a_0 = 1.0432$ nm.

3.3. Microstructural observation

The microstructure of the compacts fired at 650 °C for 30 d prepared by solid-state reaction and coprecipitation is shown in Fig. 7a and b, respectively. Grains in the former sample were agglomerated and coarser than those in the latter one. In comparison the coprecipitated-sample seemed to have a more uniform microstructure.

When the pure $Pb_2FeWO_{6.5}$ prepared through coprecipitation was heated in DTA, an endothermic peak appeared at 855 °C, as shown in Fig. 8a. This peak was similar to that of the coprecipitated mixture (Fig. 3). The 855 °C peak resulted from the thermal decomposition of $Pb_2FeWO_{6.5}$. For the sample quenched at 830 °C in DTA (lower than the 855 °C peak), a large amount of $Pb_2FeWO_{6.5}$ coexisting with $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ was detected in XRD. For the sample quenched at 860 °C (higher than the 855 °C peak), all of $Pb_2FeWO_{6.5}$ decomposed and only $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ appeared.

The microstructure of the fracture surfaces for these two samples are shown in Fig. 8b and c. There was a drastic change in microstructure between the samples cooled at 830 and 860 °C. After complete decomposition at 860 °C, only agglomerated $PbWO_4$ grains and $PbFe_{2/3}W_{1/3}O_3$ grains with a larger size could be observed.

TABLE I Powder X-ray diffraction data of $Pb_2FeWO_{6.5}$

hkl	d_{obs} (nm)	d_{calc} (nm)	I/I_0
111	0.6009	0.6023	2
200	0.3693	0.3688	< 1
311	0.3147	0.3145	4
222	0.3013	0.3011	100
400	0.2609	0.2608	33
331	0.23932	0.23932	5
422	0.21295	0.21293	< 1
{333 511	0.20071	0.20075	2
440	0.18443	0.18440	30
531	0.17633	0.17632	< 1
622	0.15725	0.15726	25
444	0.15054	0.15057	7
800	0.13041	0.13039	3
662	0.11964	0.11966	7
840	0.11663	0.11663	6

4. Discussion

Comparing the diffraction data given in Table I with those of the pyrochlore phase which is formed with $PbFe_{2/3}W_{1/3}O_3$ in the solid-state reaction of $3PbO–Fe_2O_3–WO_3$ [9], the lattice spacings and intensities of both results are similar. A new spacing (6 2 2), however, is found in this work. The absence of the (6 2 2) diffraction peak in the previous report [9] is considered to be caused by the overlap of the (6 2 2) spacing of the pyrochlore phase with the (3 1 1) spacing of $PbFe_{2/3}W_{1/3}O_3$. Based on the data obtained from $Pb_2FeWO_{6.5}$, the lattice constant is refined to be $a_0 = 1.0432$ nm.

Because no superlattice line could be found in the X-ray diffraction pattern of $Pb_2FeWO_{6.5}$, iron and tungsten cations are considered to be distributed in a disordered arrangement at the B sites of $A_2B_2O_7$, similar to the iron and tungsten cations at the B sites of $PbFe_{2/3}W_{1/3}O_3$ in terms of ABO_3. $Pb_2FeWO_{6.5}$ might have a vacant site at half of the oxygen positions as in the $Pb_2(M_{0.5}Sb_{1.5})O_{6.5}$ and $Pb_2(MSb)O_{6.5}$ systems [11–13].

Agranovskaya [1] postulated that the composition of the pyrochlore phase formed with $PbFe_{2/3}W_{1/3}O_3$

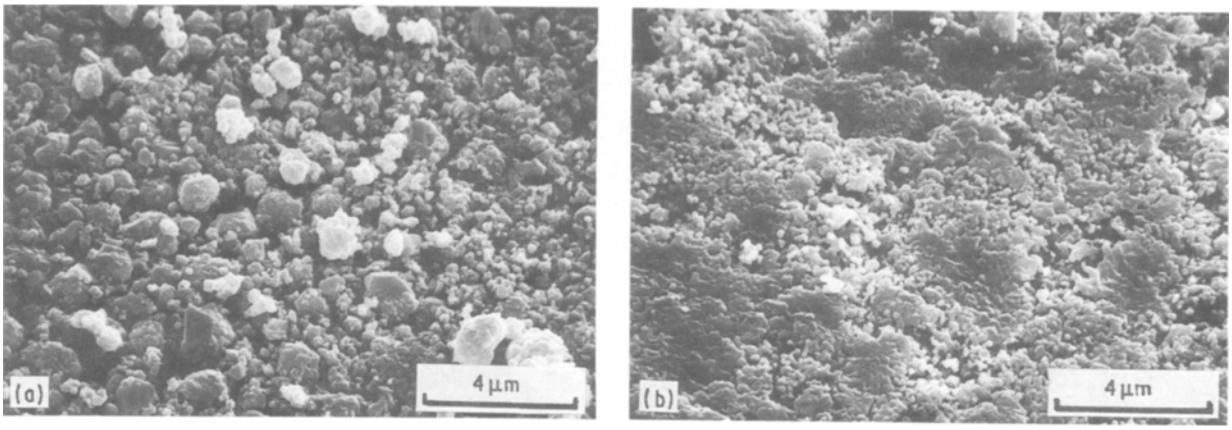

Figure 7 Scanning electron micrographs of (a) $4PbO–Fe_2O_3–2WO_3$ and (b) coprecipitated compacts soaked at 650 °C for 30 d.

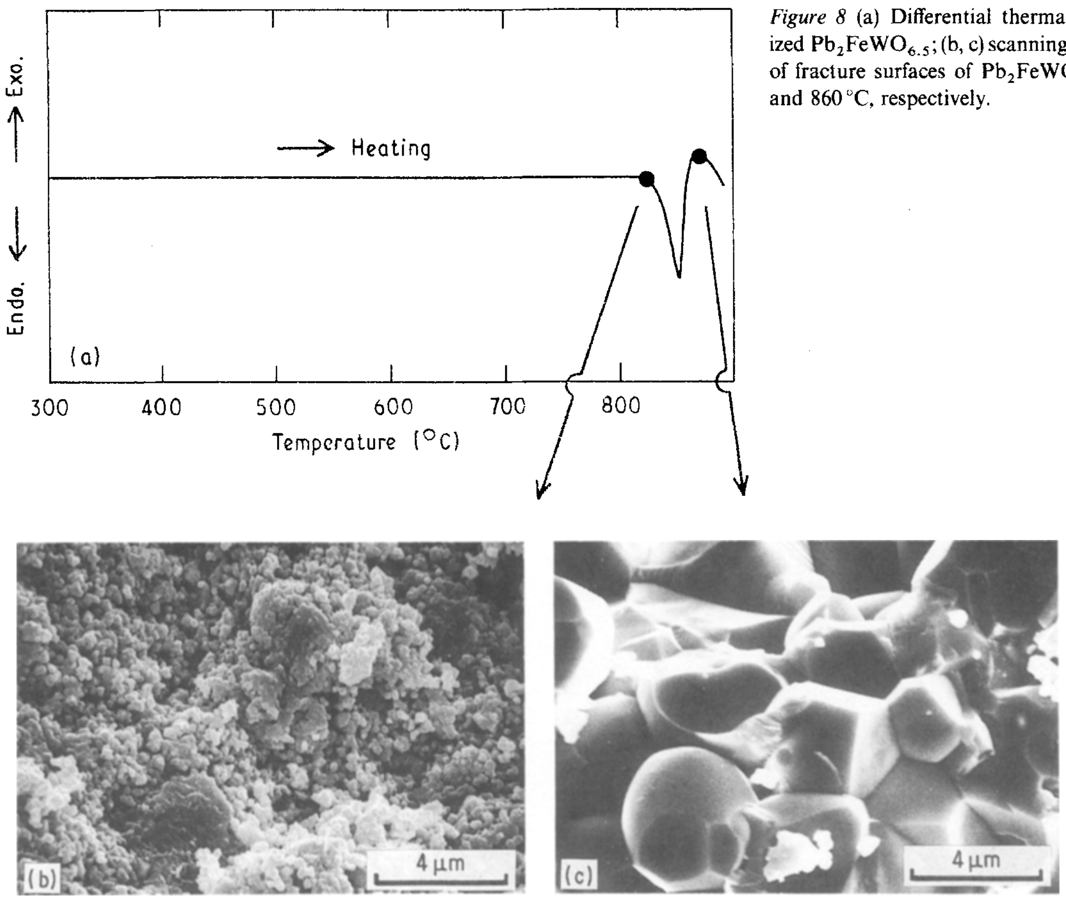

Figure 8 (a) Differential thermal analysis of synthesized $Pb_2FeWO_{6.5}$; (b, c) scanning electron micrographs of fracture surfaces of $Pb_2FeWO_{6.5}$ quenched at 830 and 860 °C, respectively.

should be $Pb_2Fe_{2/3}W_{4/3}O_7$. To verify whether this assumption was true, a coprecipitated mixture was prepared at an atomic ratio of Pb:Fe:W = 3:1:2. When heated from 600 to 690 °C, only $Pb_2FeWO_{6.5}$ and $PbWO_4$ were found to exist in samples with strong X-ray diffraction intensities. Clearly, a pure pyrochlore compound could not be produced from this composition. The coprecipitated powder mixed as Pb:Fe:W = 3:1:2 seems to react as follows

$$(Pb_3FeW_2)O_{10.5} \rightarrow Pb_2FeWO_{6.5} + PbWO_4 \quad (1)$$

Thus, the composition of the pyrochlore phase is confirmed to be not as given in Agranovskaya's report.

On heating samples prepared either from solid-state reaction or coprecipitation, the formation of the pyrochlore phase in both cases could not directly result from the constituent materials, but passes through other reaction routes of intermediate compounds. Because large amounts of $PbWO_4$ and Pb_2WO_5 are easily produced at low temperatures and the reactivity of Fe_2O_3 with other compounds is poor in the solid-state reaction, the reaction of $Pb_2FeWO_{6.5}$ will be retarded and the entire formation is difficult to achieve even through prolonged soaking.

Comparing Figs 4 and 2, the intermediate compounds in the reactions are greatly reduced in coprecipitation, implying that simpler reaction sequences have proceeded. The formation temperature of pyrochlore (450 °C) is lower in coprecipitation than in the solid-state reaction (600 °C). As is seen in Fig. 4, $PbWO_4$ predominantly reacts to yield directly $Pb_2FeWO_{6.5}$ rather than Pb_2WO_5, which is different from in the solid-state reaction. Iron-containing phases in coprecipitation may have a higher reactivity with $PbWO_4$ than Fe_2O_3 in the solid-state reaction to bypass the formation of Pb_2WO_5 and to form $Pb_2FeWO_{6.5}$ directly. From micrographs of fired soaked samples (Fig. 7a and b), a more uniform microstructure is observed in the coprecipitated samples. Atomic-scale mixing of the components is considered to be attained in coprecipitation. Consequently, the improved homogeneity and enhanced reactivity in coprecipitation will decrease the diffusion path, to induce the reaction of $Pb_2FeWO_{6.5}$ to begin at low temperatures and progress to completion.

The decomposition of $Pb_2FeWO_{6.5}$ to form $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ begins at 700 °C and is completed at 860 °C. This reaction can be expressed well on a balanced stoichiometric equation as

$$2Pb_2FeWO_{6.5} \rightarrow 3PbFe_{2/3}W_{1/3}O_3 + PbWO_4 \quad (2)$$

Based on the semi-quantitative analysis through the X-ray diffraction study, the molar ratio of $PbFe_{2/3}W_{1/3}O_3$ and $PbWO_4$ in decomposed samples was nearly equal to 3:1, which is consistent with Equation 2. Thus, this reaction is concluded to progress in the decomposition of $Pb_2FeWO_{6.5}$. A large amount of endothermic heat occurring at 855 °C in the decomposition is observed in Fig. 8a. This is considered to be related to the drastic change in microstructure (Fig. 8b and c) after the complete decomposition of $Pb_2FeWO_{6.5}$.

As a result, only the coprecipitation technique and not the solid-state reaction, can successfully be used to synthesize the pure phase of $Pb_2FeWO_{6.5}$. This compound is found to be formed at 650 °C through long soaking, but is easily decomposed when heated above 700 °C. The proper mixing process and the optimum conditions of heating treatment are essentially important for the synthesis of $Pb_2FeWO_{6.5}$.

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