

Mechanochemical synthesis of Pb_2MgWO_6 piezoceramics with alloying additives

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Abstract. Pb_2MgWO_6 was prepared using mechanochemical activation and sintering in a temperature range of 600-1000°Ñ in three ways: 1) from oxides of the corresponding metals, 2) using MgWO_4 precursor; and 3) in the presence of over-stoichiometric amounts (1wt.% and 2wt.%) of Li_2CO_3 alloying additive.

1 Introduction

Pb_2MgWO_6 piezoceramics has drawn particular attention because it can be used for the development and production of functional materials, such as Pb_2MgWO_6 -based solid-state drives and solid solutions with the degree of order in the composite controlled by mechanical activation (m/a) [1, 2]. Pb_2MgWO_6 is supposed to have a perovskite structure, while the presence of impurities worsens electro physical properties of this ceramics.

2 Experimental part

Pure WO_3 , MgO , PbO oxides, and Li_2CO_3 were used as the initial reagents for Pb_2MgWO_6 synthesis. In each case, the amount of lead oxide was 3 wt.% over stoichiometry [3]. Mechanical activation of the mixture was carried out in a planetary ball mill, AGO-2, equipped with steel jars and balls ($d = 8$ mm, $m = 200$ g, ball acceleration 40 g). To prevent iron milling, pre-lining of the balls and jars was carried out [4]. The samples were formed as pellets with $h = 2$ mm and $d = 10$ mm under a pressure of 10 t/cm² in the absence of a plasticizing agent. Sintering of the samples was carried out in a furnace PVK-1.4-8 using a heating rate of 10 °C/min. The samples were cooled down in the furnace after it was turned off. Weighting was carried out using UW220H SHIMATZU scales with 0.001g accuracy; geometrical size was measured with a micrometer with 0.01 mm accuracy. XRD patterns of the samples obtained were recorded on DRON-3 and Bruker D8 Advance powder diffractometers.

Synthesis of the precursor: WO_3 and MgO samples were activated in the mill for 10 min, and then sintered at 900°C for 4 hours. Later on, the as-prepared MgWO_4 was milled and used in the synthesis of the samples.

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3 Results and discussion

Method 1: Synthesis of Pb_2MgWO_6 from initial oxides (WO_3 , MgO , PbO).

According to the XRD data, immediately after m/a of the oxides, a two-phase system, consisting of cubic Pb_2MgWO_6 S.G. Fm-3m (no.225) and tetragonal $PbWO_4$ S.G. I41/a (no.88) modifications, is formed. $PbWO_4$ is well crystallized and its structure remains unchanged up to 800 °C (Fig. 1).

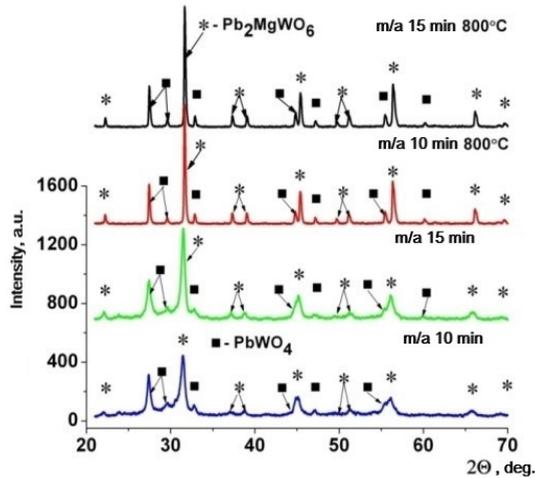


Fig. 1. XRD patterns of the samples after m/a for 10 and 15 min and sintering at 800°C.

After polishing the samples, this phase does not disappear, therefore, the structure is uniform throughout the sample thickness. After sintering at 950°C, the amount of $PbWO_4$ phase decreases drastically, and monoclinic modification of the Pb_2WO_5 phase S.G. C2/m (no.12) appears in the sample, which remains unchanged throughout all ranges of the samples (Fig. 2). MgO is a part of the forming solid solutions and its reflections do not appear in the XRD patterns.

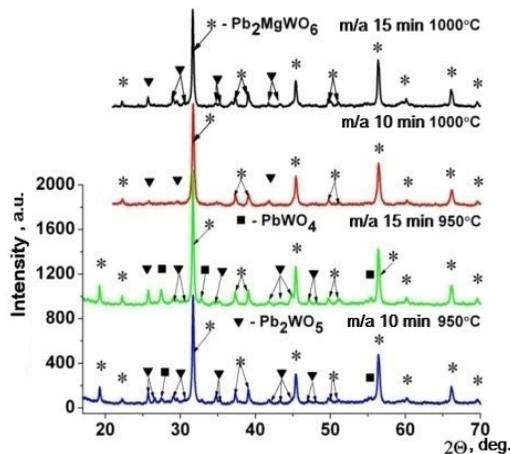


Fig. 2. XRD patterns of the samples after m/a for 10 and 15 min and sintering at 950 and 1000°C.

Fig. 3 shows the density of the samples as a function of sintering temperature. The highest density, 8.64 g/cm³, was obtained after m/a for 30 min at a sintering temperature of 900°C.

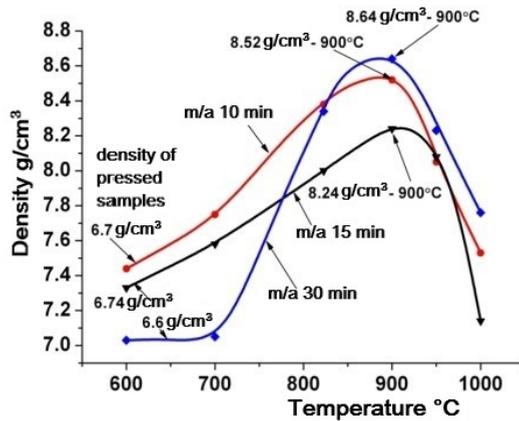


Fig. 3. The density of the samples in the sintering temperature range of 600-1000°C.

Method 2: Synthesis of Pb_2MgWO_6 using $MgWO_4$ precursor

In this case, immediately after mechanochemical activation, Pb_2MgWO_6 is formed. An increase in the sintering temperature results in a decrease in the amount of this phase and the appearance of the Pb_2WO_5 phase (Fig. 4). This mechanism is reported in studies [5, 6].

Figures 4 and 5 show reflections of the Pb_2MgWO_6 (asterisks) and Pb_2WO_5 phases. As seen, at 600°C, a two-phase system consisting of Pb_2MgWO_6 and Pb_2WO_5 (Fig. 4) is formed, while at 800°C and 900°C, Pb_2WO_5 and Pb_2MgWO_6 respectively are formed (Fig. 5).

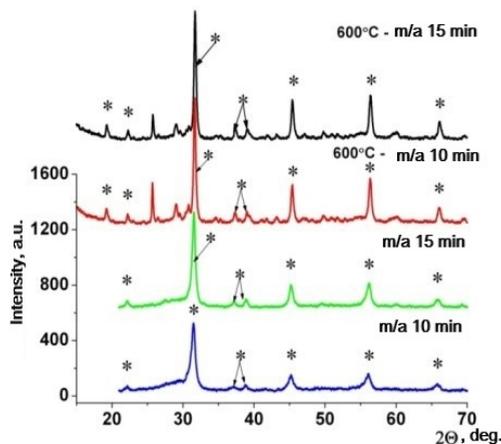


Fig. 4. XRD patterns of the samples after m/a for 10 and 15 min and sintering at 600°C.

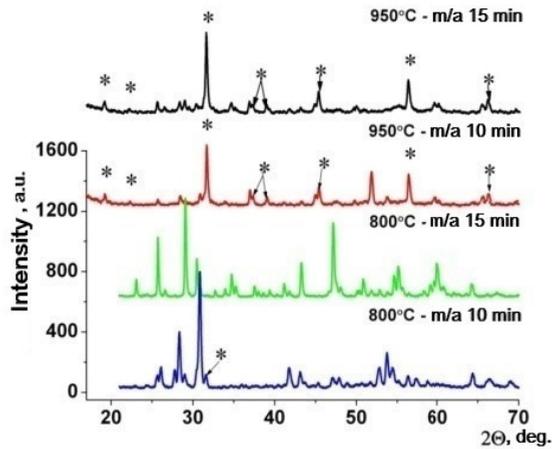


Fig. 5. XRD patterns of the samples after m/a for 10 and 15 min and sintering at 800 and 950°C.

As seen from Fig. 6, the density of the sample obtained after m/a for 15 min and sintering at 700°C is 8.73 g/cm³. For comparison, when synthesizing from oxides, after m/a for 15 min, the densest sample (8.24 g/cm³) is achieved at 900°C.

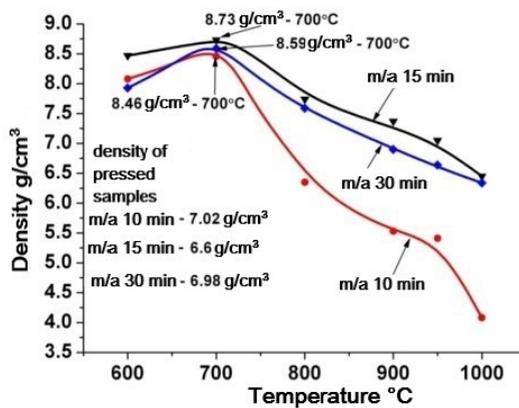


Fig. 6. The density of the samples in the sintering temperature range 600-1000°C.

Method 3: Study of the influence of alloying with lithium on sintering

A) 1 and 2 wt.% Li₂CO₃ were added to Pb₂MgWO₆ synthesized from the oxides. After m/a, a two-phase system consisting of Pb₂MgWO₆ and PbWO₄ is formed. After sintering the samples in the presence of 1% Li₂CO₃ at 600 °C, the Pb₂WO₅ phase appears, while in the presence of 2 wt.% Li₂CO₃, the PbWO₄ phase remains in the sample (Fig. 7).

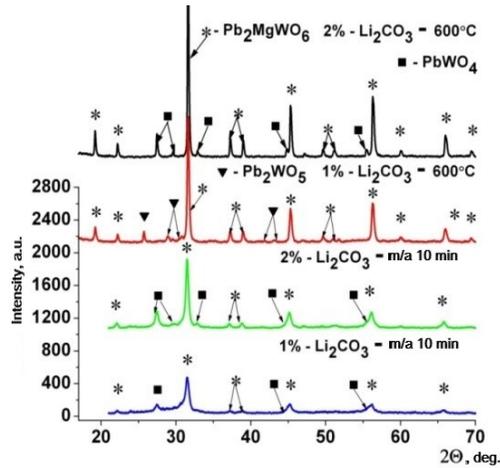


Fig. 7. XRD patterns of the samples obtained in the presence of 1 and 2 wt.% Li_2CO_3 , at 600°C.

After sintering at 800°C, the phase ratio is the same, while sintering at 1000°C results in the formation of almost Pb_2MgWO_6 phase alone (Fig. 8).

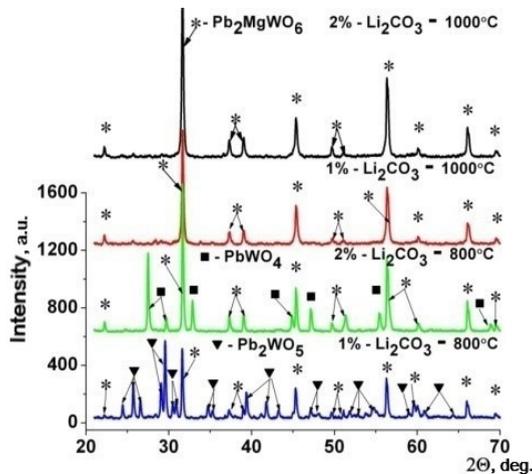


Fig. 8. XRD patterns of the samples obtained in the presence of 1 and 2 wt.% Li_2CO_3 , at 800 and 1000°C.

In the presence of 1 wt.% Li_2CO_3 , the densest samples (8.63 g/cm^3) were obtained at 700°C, while in the presence of 2 wt.% Li_2CO_3 , the maximum density, 8.48 g/cm^3 , is achieved at 1000°C (Fig. 9).

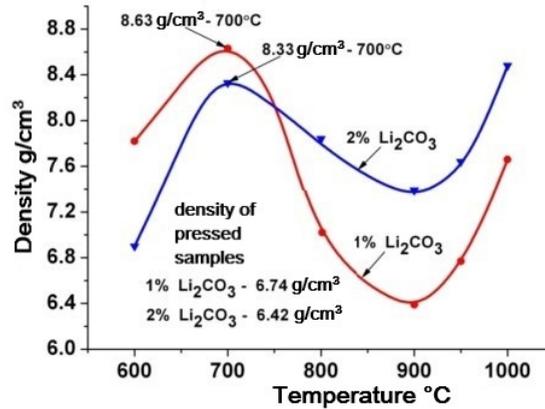


Fig. 9. The density of the samples obtained in the presence of 1 and 2 wt.% Li₂CO₃.

B) 1 and 2 wt.% Li₂CO₃ were added to Pb₂MgWO₆ synthesized from precursor. After m/a, at the initial sintering stages, the samples almost did not contain any impurity phases. At higher sintering temperatures, both in the presence of 1% and 2% Li₂CO₃, Pb₂WO₅ appeared as the second phase. After sintering at 1000°C in the presence of 2 wt.% Li₂CO₃, only Pb₂MgWO₆ perovskite phase was obtained (Fig. 10).

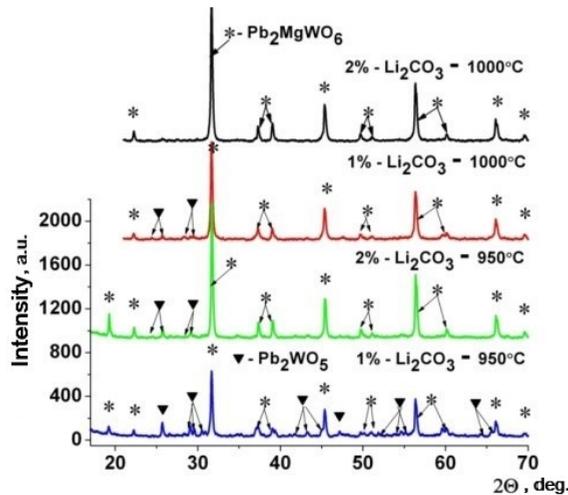


Fig. 10. XRD patterns of the samples obtained in the presence of 1 and 2 wt.% Li₂CO₃, m/a for 10 min, sintering at 950 and 1000°C.

Fig. 11 shows the dependence of the density of the samples on sintering temperature in the range from 600 to 1000°C. In both cases, the highest density is achieved at 700°C. Then it decreases as the temperature increases from 700 to 900°C and it again increases as the temperature increases from 900 to 1000°C. The densities of the samples obtained at 700°C in the presence of 1 wt.% and 2 wt.% Li₂CO₃ were 8.33 and 8.63 g/cm³ respectively.

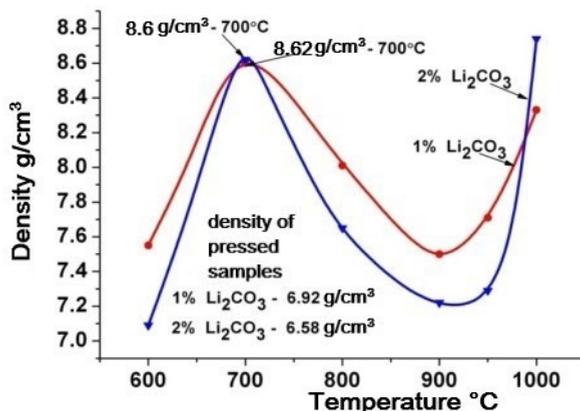


Fig. 11. The density of the samples obtained in the presence of 1 and 2 wt.% Li₂CO₃.

4 Conclusion

Pb₂MgWO₆ was prepared from oxides of the corresponding metals (method 1) and from MgWO₄ precursor (method 2) using mechanochemical activation and sintering in a temperature range of 600-1000°C. In the first case, the densest samples (8.64 g/cm³) were obtained after m/a for 30 min and sintering at 900°C, while in the second case, the highest density (8.73 g/cm³) was achieved at 700°C and at activation for 15 min. The addition of lithium alloying improves the quality of the samples. In both cases, the densest samples were obtained in the presence of 1 wt.% or 2 wt.% Li₂CO₃ at 700°C and 1000°C respectively. The decrease in the density in the temperature range 700-900°C is due to (1) the formation of three-phase system with different lattice parameters (PbWO₄, Pb₂WO₅ and Pb₂MgWO₆), (2) decomposition of lithium carbonate, and (3) an increase in the lead oxide vapor pressure. Pure perovskite phase was obtained during sintering at 1000°C in the presence of 2 wt.% Li₂CO₃ and in the presence of over-stoichiometric amounts (1wt.% and 2wt.%) of Li₂CO₃ alloying additive.

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