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Pressure-induced crystallite breaking in $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids

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Abstract In the compacting process of the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids under the pressure range of 0.0—4.5 GPa, the apparent pressure-induced crystallite breaking phenomenon in these nanosolids was observed. With increasing pressure up to 4.5 GPa, the average grain size decreases by 46% while the magnetization of nanosolids decrease by 40% and their coercive increases by 35%. This kind of breaking has a close relation to the existence of oxygen deficiency in $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanoparticles. A simple and convenient method for preparing the bulk nanosolids with a large number of clean interfaces has been suggested.

Keywords: nanosolid, pressure-induced breaking, high pressure.

IN general, the pressure-induced crystallite breaking (PICB) phenomenon will occur to a certain degree in solid material under high pressure up to several GPa, but this PICB effect in most of materials is usually so weak that it can be disregarded. However, the PICB effect could be very strong in some brittle matter. There have been only few reports published about this subject so far. Liu *et al.*[1] found that the grains of SrB_2O_4: Eu^{2+} polycrystalline material were broken from micrometers to nanometers under high pressure, but the effect of PICB on the properties of material had not been investigated. Williamson *et al.*[2] found that the grain size of α-Fe_2O_3 polycrystalline materials is reduced from 200 to 60 nm under the shock pressure of 8—27 GPa, and studied the influence of the decrease of grain size and the increase of defect on their Morin transition temperature by Mössbauer spectroscopy and magnetic measurement. Therefore, it will be very interesting to study the PICB effect on solid materials because a lot of new interfaces will form inside the materials in the compacting process, and then the properties and microstructure of materials will be changed strongly. In particular, it may be more interesting in the case of nanometer crystalline solid (nanosolid) materials because the number of interfaces in nanosolid which has been large enough can increase further in the PICB process, and this may lead to the improvement of their properties.

1 Experimental procedure

The $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanoparticles were synthesized by sol-gel method described in ref. [3]. The $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids were prepared by compacting the nanoparticles in a high pressure chamber of a belt type of press under the pressure range of 0.0—4.5 GPa. The pressure was measured by the method described in ref. [4]. The crystal structure and grain size of samples were determined by X-ray diffraction (XRD). The interface atomic state and magnetic properties of nanosolids with compacting pressure were studied by Mössbauer spectroscopy and magnetic measurement.

2 Results and discussion

The XRD patterns of the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanoparticle and the nanosolid compacted at 4.5 GPa as an example measured are shown in fig. 1. The crystal structure of nanoparticles was determined to belong to the cubic perovskite structure with lattice parameter of 0.388 9 nm by the analysis of their XRD pattern. It can be seen from fig. 1 that all diffraction peaks become broadened obviously with increasing pressure, but their peak positions and the diffraction background do not change. The grain sizes of

nanosolids in the directions that are perpendicular to various crystal planes are listed in table 1, which were calculated by the Scherrer formula after the effects of geometry, K_{α_2} radiation and the microstrain had been deducted. In table 1, the grain sizes in every crystal direction all decrease significantly and the average grain size of nanosolid decreases from 26 to 14 nm with the increase of pressure from 0.0 to 4.5 GPa. Therefore, we have a conclusion that the obvious PICB phenomenon has occurred in the compacting process of nanosolids while the crystal structure in nanoparticles does not change.

Table 1 The grain sizes in various crystal directions D_{hkl} and the average grain size D_0 of the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids under different pressures

D_{hkl} P/GPa	D_{110} /nm	D_{111} /nm	D_{200} /nm	D_{211} /nm	D_0 /nm
0.0	30	30	24	20	26
1.0	22	22	14	12	17.5
3.0	18	18	12	10	14.5
4.5	18	18	10	10	14

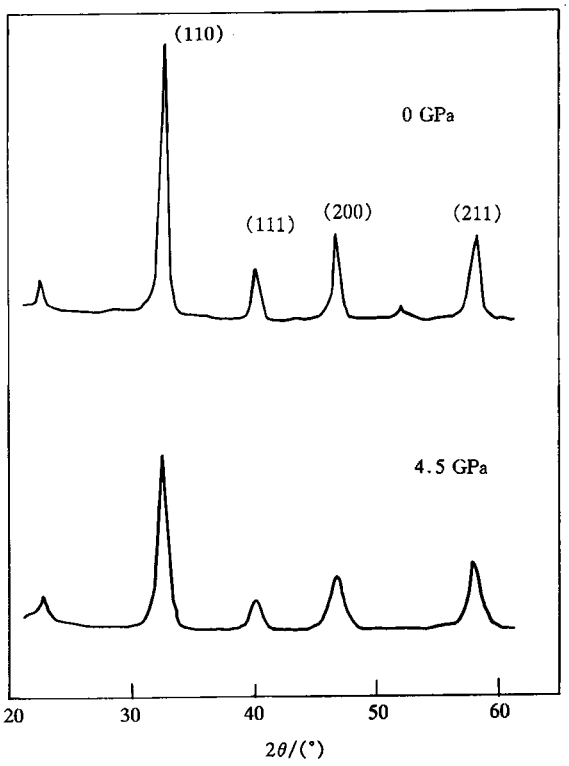

Fig. 1. The XRD patterns of (a) $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanoparticles and (b) only the nanosolid compacted at 4.5 GPa.

It can be found from table 1 that the crystallites were broken most seriously in the (200) plane. The grain size in the [200] direction decreases by 58% under 4.5 GPa. Because the crystal structure of nanoparticles is cubic, their atomic configuration may be considered to be similar to that of the standard ABO_3 cubic perovskite structure. In this structure, (200) is just the crystal plane in which the density of oxygen atom is the largest. Because there is a certain number of oxygen deficiencies in the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ lattice due to the substitution of Sr^{2+} for La^{3+} and their number can be increased by high pressure[5], the density of oxygen deficiency is also the largest in the (200) plane of $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ crystal structure. Therefore, it is reasonable to believe that the existence of the oxygen deficiencies may have an important effect of growth center for cleavage crack on the occurrence of PICB in nanosolids, though the grain break is mainly determined by the crystal structure and the bonding form of nanosolid. This viewpoint is supported by the fact that we had not found any obvious PICB phenomena in the $LaMnO_3$ nanosolids under pressure up to 4.0 GPa, which have the average grain size of 51 nm and were prepared by the same method as that of $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolid, because there is a very few oxygen deficiencies in $LaMnO_3$ crystal. However, further work needs to be done to make clear the nature of the effect of oxygen deficiency on the PICB process of $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids.

In order to study the effect of PICB on the microstructure and properties of $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids, we measured their magnetic properties and Mössbauer spectrum at room temperature as shown in fig. 2. All spectra exhibit a single quadrupole doublet and can be fitted by two subspectra. Though the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ crystal usually has weak ferromagnetism due to the superexchange interaction of Mn^{3+}-O-Mn^{4+} because there are a lot of Mn^{4+} ions in the crystal caused by the substitution of Sr^{2+} for La^{3+} [6], the Mössbauer spectra of samples do not show the magnetic split lines. This characteristic of these Mössbauer spectra is caused by the small-size effect and the substitution of Fe^{3+} in the samples. The fitting parameters are listed in table 2. One subspectrum with lager quadrupole is due to the absorption of the Fe atoms lying in interface, and the other one with smaller quadrupole is due to the Fe atoms located inside grains because the crystal symmetries of the former atoms are lower than those of the latter ones[7].

In table 2, the relative area (1) of the subs pectrum of interface atoms increases from 31.0% to 42.2% with increasing pressure from to 0.0 to 4.5 GPa. This increment reflects the formation of a large number of new interfaces in the compacting process. Meanwhile, the quadrupole splitting value QS (1) of interface atoms increases rapidly with pressure. This is mainly due to the increase of interface atoms and the rearrangement of interface atoms under high pressure, including the change of the state of some surface atoms among grains from free to asymmetric coupling state, which can make the quadrupole value increase.

The measurement results of specific saturation magnetization (δ_s) and coercive force (H_c) of $La_{0.7}$-$Sr_{0.3}$ $Mn_{0.9}$ $Fe_{0.1}$ O_3 nanosolids are listed in table 3. Clearly Ms decreases and H_c increases greatly with increasing pressure. The variations of Ms and H_c are caused by the decrement of the grain size in the compacting process. This size effect is just as observed in other nanoparticles[8, 9]. The decrement of Ms is mainly due to the reduction of superexchange interaction in nanosolids because of the breaking of some Mn^{3+}-O-Mn^{4+} bonds inside crystallites and the formation of many magnetic disorder interfaces. In the PICB process, there is a very strong effective anisotropy on the interface and surface of crystallites in nanosolid because of the serious crystallite breaking. This will lead to the appearance of the disorder canting spin moment and the formation of a lot of magnetic disorder interfaces. The increment of H_c is caused by the transformation of magnetic structure from polydomain to single domain with the reduction of grain size[9].

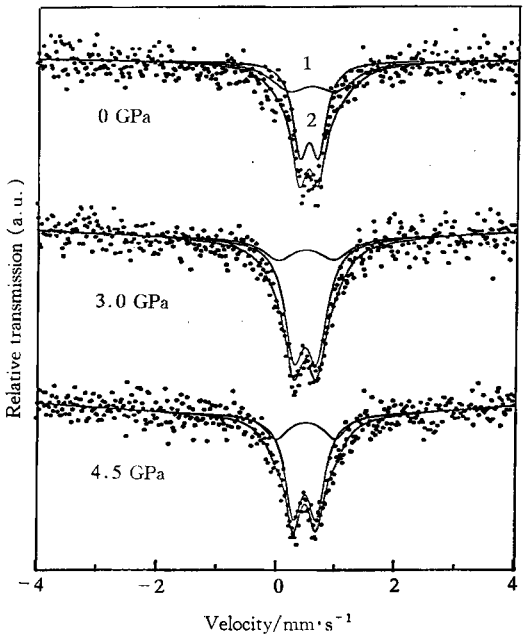

Fig. 2. ^{57}Fe Mössbauer spectra of $La_{0.7}$ $Sr_{0.3}$ $Mn_{0.9}$ $Fe_{0.1}$ O_3 nanosolids under different pressures. The velocity was calibrated with an α-Fe foil. The radiation resource is ^{57}Co/Rh.

Table 2 Mössbauer parameters of the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids under different pressures

P/GPa	0.0	3.0	4.5	P/GPa	0.0	3.0	4.5
IS(1)/mm·s^{-1}	0.229	0.229	0.253	IS(2)/mm·s^{-1}	0.234	0.236	0.248
QS(1)/mm·s^{-1}	0.768	1.004	1.017	QS(2)/mm·s^{-1}	0.314	0.389	0.389
A(1) (%)	0.316	0.357	0.422	A(2) (%)	0.684	0.643	0.578

IS is the isomer shift, QS is the quadrupole splitting, and A is the relative subspectrum area.

Table 3 δ_s and H_c values of $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids under different pressures

P/GPa	0.0	3.0	4.5
$\delta_s \times 10^{-4}$/T	67.13	45.29	40.64
H_c/A·m^{-1}	5625	6963	7616

As a conclusion, the PICB phenomenon occurred obviously in the compacting process of the $La_{0.7}$-$Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids. Under the pressure of 4.5 GPa, the average grain size of nanosolid has decreased by 46% while their microstructure and magnetic property were changed strongly. Therefore, this PICB effect of the $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$ nanosolids may provide us a new simple and convenient way to prepare the bulk nanosolid material with clean interfaces. In practice, we can select some brittle solids as raw materials in which there are a large number of defects in the lattice, and then compact them into a bulk shape nanosolid materials only under high pressure. On the other hand, it is also very important to study the nanosolids prepared by this method because their interfaces are formed directly by the breaking of perfect lattice and these interfaces are completely different from those of the nanosolid prepared by com-

pacting nanoparticles.

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Wave-packet method for instability of three-dimensional boundary layer of swept wing

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Abstract A wave-packet method is proposed to study evolution the behavior of disturbances in 3-D boundary layer on a swept plate. It is proved that the constant-phase lines are equivalent to the streaks observed in flow-visualization experiment and the asymptotic solution of wave-packet equation can give accurate conditions for e^N method.

Keywords: swept plate, wave packet, structure of streaks.

THE stability theory of laminar flow is a basis for laminar flow prediction and control. However, it is only analyzing the evolution behavior of the monochromatic wave, and the e^N method which is used in predicting transition of laminar boundary layer is based on linear stability theory. It is effective to predict the transition of two-dimensional boundary layer at low level of turbulence, but there exist some problems in three-dimensional boundary layer[1]. Using different e^N methods, Radeztsky *et al.* calculated the amplitude amplification factors of stationary vortices of three-dimensional boundary layer, and no result is consistent with experimental data[2]. The reason is that it is unclear how to define the most unstable disturbance in three-dimensional boundary layer and how to determine its growing path. Streaks observed in flow visualization are theoretically called instability of cross flow, a stationary vortex in stream direction. Nitchke-Kowsty and Bippes carefully measured the streak structure of boundary layer on a swept plate, and found that the angle of the streak with potential flow direction is 3°—5°[3]. Generally, the streaks are considered as the constant phase lines of the most unstable waves. In fact, natural disturbances excite a broad spectrum of waves throughout the flow, and this leads to modulation of a wave packet with different frequencies and orientations. So the streaks are corresponding to a constant phase line of wave packet rather than monochromatic wave. As a theory of predicting transition, to analyze the evolution behavior