Raman Spectra from Laser-Processed Lead Zirconate Titanate ($PbZr_{0.3}Ti_{0.7}O_3$) Prepared by a Sol-Gel Process

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We report on investigations of laser-induced crystallization of $PbZr_{0.3}Ti_{0.7}O_3$ (PZT) gel-powder. By means of micro-Raman spectroscopy, and of optical and scanning electron micrography (SEM), we show that, upon laser irradiation, amorphous PZT material is transformed into microcrystals of the perovskite structure. It was found that the laser-induced crystallization is much faster than crystallization through calcination in a conventional oven.

Index Headings: **Raman spectroscopy; PZT; Laser processing.**

INTRODUCTION

The solid solution $PbZr_{1-x}Ti_xO_3$ (named PZT) between antiferroelectric $PbZrO_3$ and ferroelectric $PbTiO_3$ is a piezoceramic compound which crystallizes in the perovskite structure. Its dielectric and piezoelectric properties make this ceramic very useful in the electronics industry. The piezoelectric activity reaches a maximum when ceramic compositions are close to the morphotropic phase boundary between the rhombohedral and tetragonal modification. This morphotropic phase boundary exists for $x = 0.46$.[1]

The production of high-quality technical ceramics requires more extensive control of powder characteristics than is possible by conventional ceramic processing methods (e.g., by the mixed-oxide route). Important powder characteristics include: (1) particle-size distribution and morphology, and (2) chemical purity and composition. For example, heterogeneities in chemical distribution can degrade electrical performance characteristics. Therefore, in order to prepare materials of uniform composition on a microscopic scale, a variety of chemical methods[2,3] of preparation have been used, among them the sol-gel processing of metal alkoxides.[4] The sol-gel process involves the dissolution of the precursor materials (lead acetate along with the zirconium and titanium alkoxides) in methanol, hydrolysis and polycondensation in the resulting solutions to form gels, and the heat treatment of these amorphous gels to form polycrystalline perovskite PZT materials. For $PbZr_{0.3}Ti_{0.7}O_3$, this phase transformation requires several hours in an oven at a temperature of 550°C.

In this paper we report on the crystallization of the amorphous gel-powder when laser processed, i.e., heated up to the melting point by means of an argon-ion laser emitting in the visible region. As will be shown below, fairly low laser powers are needed to perform crystallization. The latter can be monitored via micro-Raman spectroscopy.

EXPERIMENTAL

The lead zirconate titanate ($PbZr_{0.3}Ti_{0.7}O_3$) material was prepared according to a variation of the sol-gel procedure reported by Ostertag *et al.*[1] Lead acetate trihydrate [$Pb(OAc)_2 \cdot 3\ H_2O$] was dissolved in methanol at 65°C. Separately, zirconium propoxide [$Zr(O^nPr)_4$] and titanium ethoxide [$Ti(OEt)_4$] were mixed in the respective quantities, and acetic acid was added. The latter was found to prevent spontaneous hydrolysis and condensation of the alkoxides, probably by the formation of complexes.[1] The Zr-Ti solution was added to the dissolved lead acetate under stirring, and after 15 min water was added by drops to start hydrolysis. The viscosity of the solution increased continuously, and after a few minutes the solution was gelatinous. After drying for 24 h at 110°C, a nearly white μm-sized powder was obtained.

After various heat treatments the powder samples were pressed into pellets. Raman spectra were measured with a Dilor (Model XY) triple grating spectrometer and a multichannel analyzer (OMA) with a back-scattering arrangement. With the spectrometer in a subtractive dispersion mode, high suppression of laser stray light was achieved. The green laser line (514.5 nm) of a Spectra-Physics argon-ion laser was used in this study for all Raman measurements and also for the laser-induced crystallization process. Micro-Raman measurements and optical micrographs were obtained by means of an Olympus microscope, which has been modified for micro-Raman excitation. Powder x-ray diffraction patterns were measured with an automated Philips powder x-ray diffractometer, using Cu-Kα radiation with a single crystal graphite monochromator.

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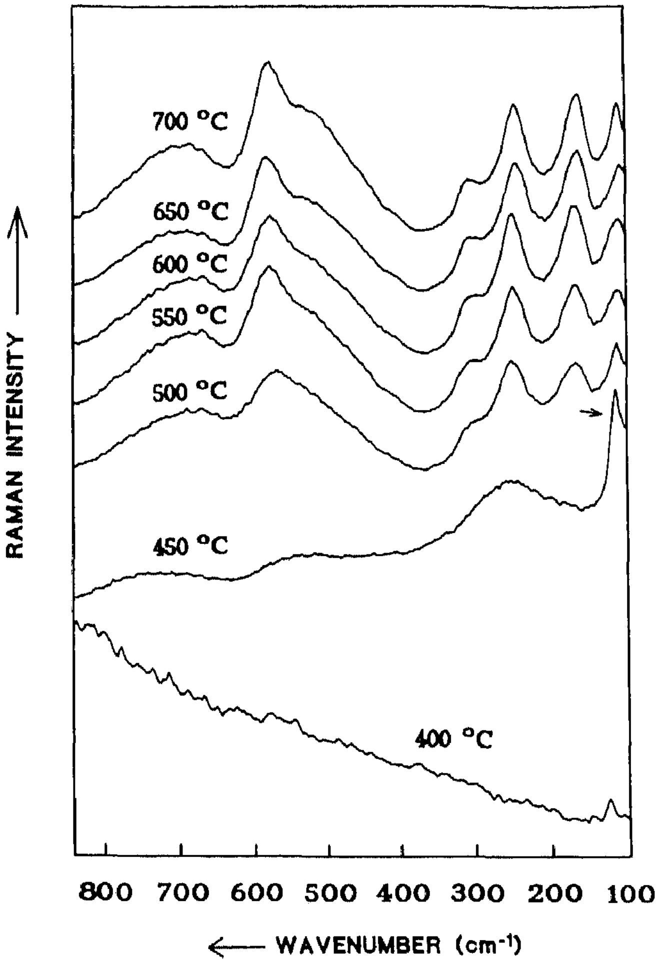

FIG. 1. Raman spectra obtained from $PbZr_{0.3}Ti_{0.7}O_3$ samples heated isochronally to various temperatures as indicated. Heat rate: 2°C/min. Duration of heat treatment: 4 h.

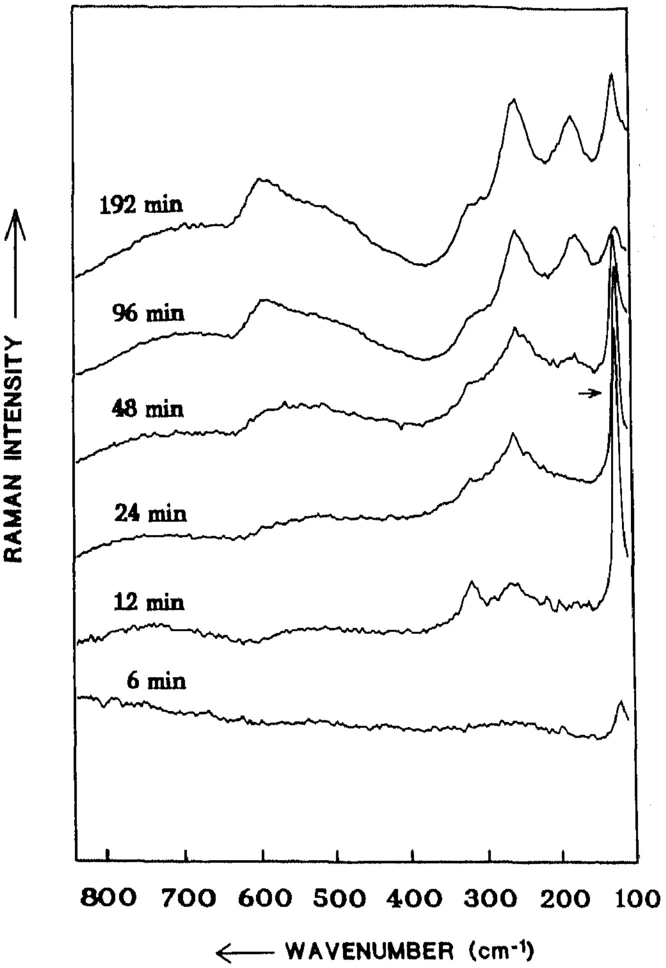

FIG. 3. Raman spectra obtained from $PbZr_{0.3}Ti_{0.7}O_3$ samples heated isothermally for different periods of times as indicated. Temperature: 550°C.

RESULTS AND DISCUSSION

In this section we first discuss the laser-induced crystallization of $PbZr_{0.3}Ti_{0.7}O_3$ and its dependence on duration and laser power density. Laser annealing of the amorphous PZT material is followed by Raman spectroscopy and optical and scanning electron micrography. For the purpose of comparison, the Raman spectra of isochronally and isothermally calcinated $PbZr_{0.3}Ti_{0.7}O_3$ gels are also shown.

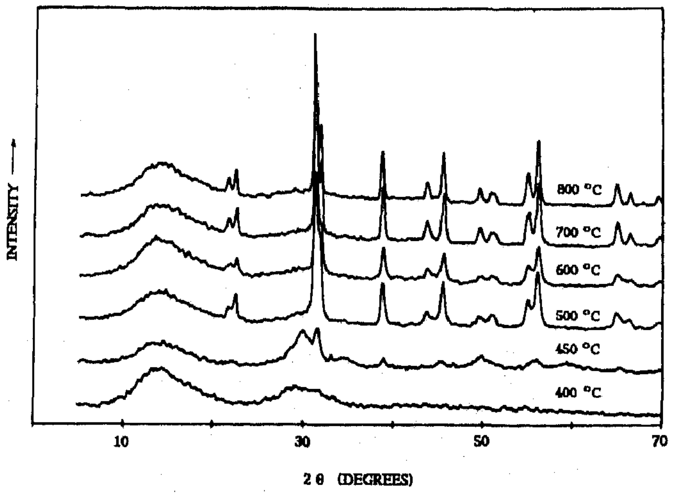

FIG. 2. Powder x-ray diffraction patterns of $PbZr_{0.3}Ti_{0.7}O_3$ samples heated isochronally to various temperatures as indicated. Heat rate: 2°C/min. Duration of heat treatment: 4 h.

Raman Spectra of Isochronally Calcinated $PbZr_{0.3}Ti_{0.7}O_3$ Gel Powders. In Fig. 1 we display room-temperature Raman spectra obtained from samples heated isochronally up to various temperatures as indicated in the figure, kept at this temperature for 4 hours and cooled down slowly to room temperature.

From the amorphous PZT samples, which had been heated isochronally up to temperatures below 400°C, we have not been able to detect Raman bands, because of strong fluorescence. This fluorescence is emitted from species as a result of burning of organic components. Samples prepared with calcination temperatures only above 400°C showed Raman bands. After heat treatment at 450°C, a Raman band could be detected at 144 cm^{-1} arising from lead monoxide (PbO) (indicated by an arrow in Fig. 1) as a consequence of phase separation. Raman bands from perovskite were first observed in our investigation only after the $PbZr_{0.3}Ti_{0.7}O_3$ gel powder was heated up to about 500°C. The bands are even more pronounced for higher calcination temperatures, and they

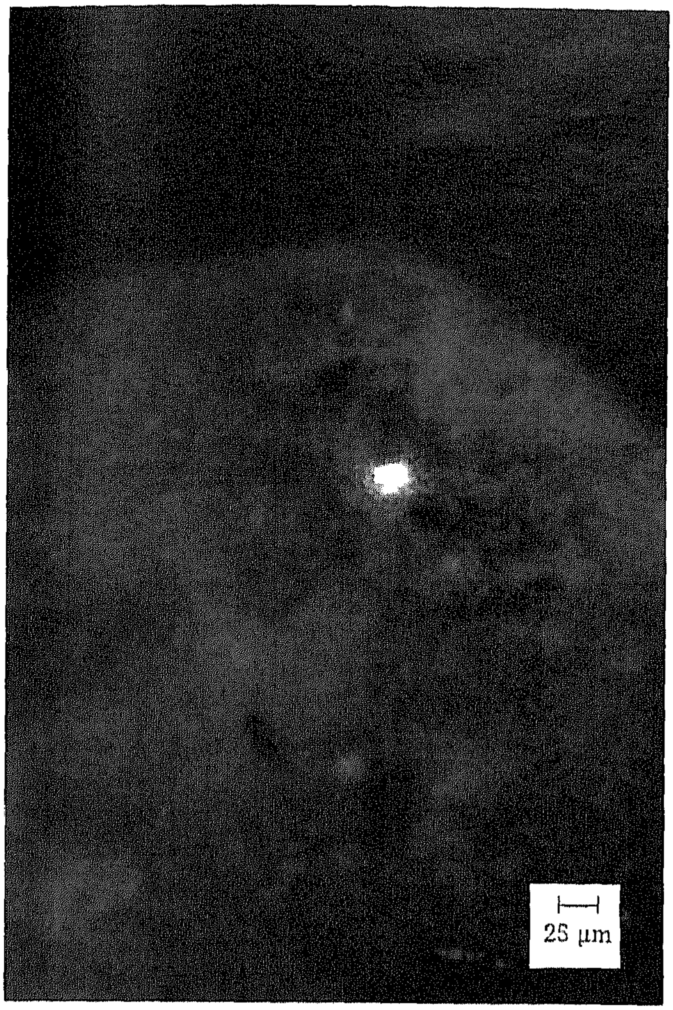

FIG. 4. Optical micrograph of phase-separated PbO on the surface of a $PbZr_{0.3}Ti_{0.7}O_3$ pellet heat treated at 700°C. The bright spot is from the incident laser which is used for Raman excitation.

get more distinct and more intense with increasing calcination temperature. The frequencies of the observed Raman lines are consistent with those reported earlier for related PZT compositions by Burns and Scott.[5]

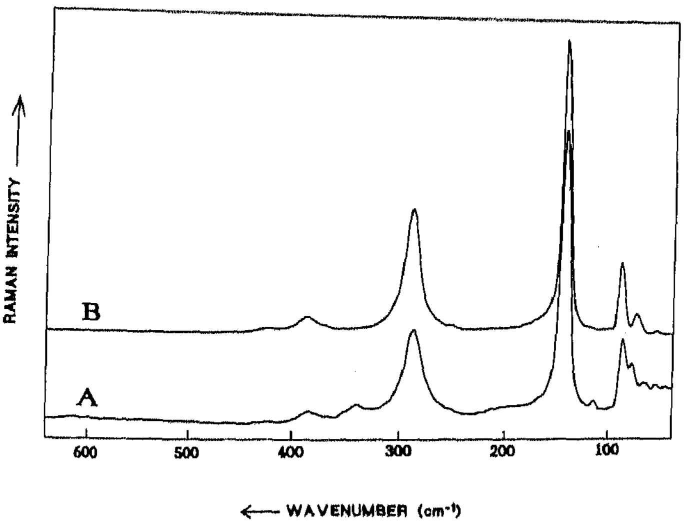

FIG. 5. (*A*) Micro-Raman spectrum of phase-separated PbO. (*B*) Micro-Raman spectrum of pure commercially available PbO.

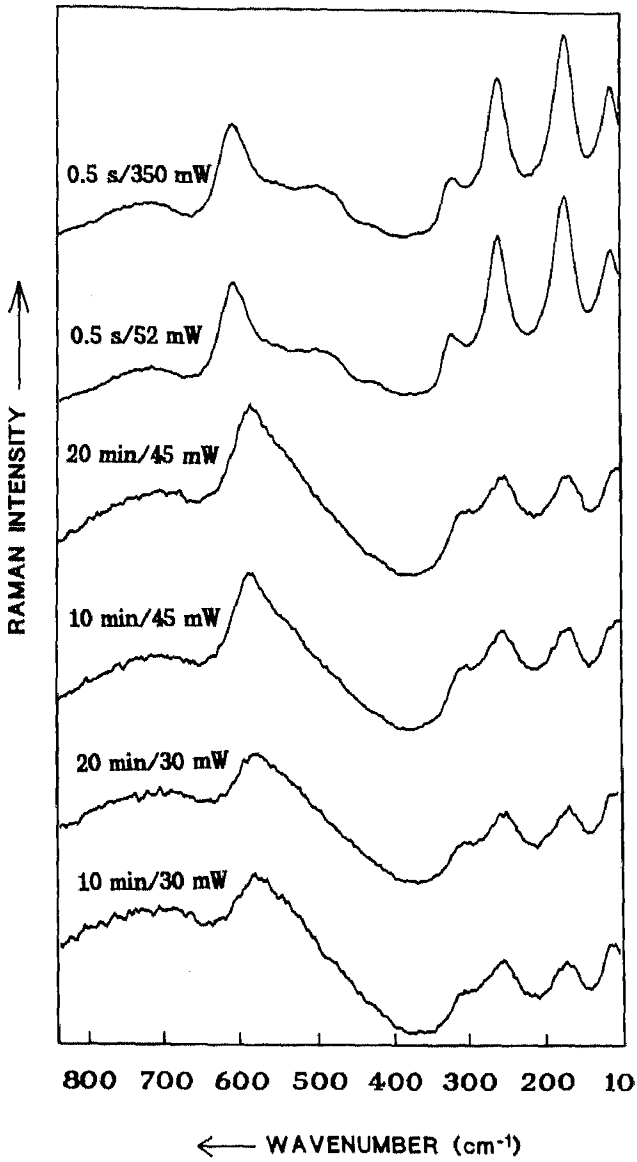

FIG. 6. Micro-Raman spectra of $PbZr_{0.3}Ti_{0.7}O_3$ samples irradiated with different laser powers for different periods of times as indicated.

Parallel to the Raman spectroscopic investigations, we performed powder x-ray scattering for the same stages of heat treatment. Figure 2 illustrates the powder x-ray diffraction patterns of the same isochronally heated samples. The prepared gels were x-ray amorphous after heat treatment below 400°C. A PbO x-ray peak can be seen at $2\Theta = 30°$ for the sample heated up to 450°C. The broad peak below $2\Theta = 20°$ is due to scattering from the sample holder.

After heat treatment above about 500°C all essential features of the crystalline perovskite material are observable; the x-ray peaks get sharper and more intensive, indicating a higher degree of crystallization.

Raman Spectra of Isothermally Calcinated $PbZr_{0.3}Ti_{0.7}O_3$ Gel Powders. The Raman spectra of isothermally heated $PbZr_{0.3}Ti_{0.7}O_3$ gel powders are shown in Fig. 3. The samples are heated up to 550°C and kept at this temperature for different periods of times. At up to 24 min, the spectra are rather featureless as far as the perovskite phase is concerned, but a strong Raman peak

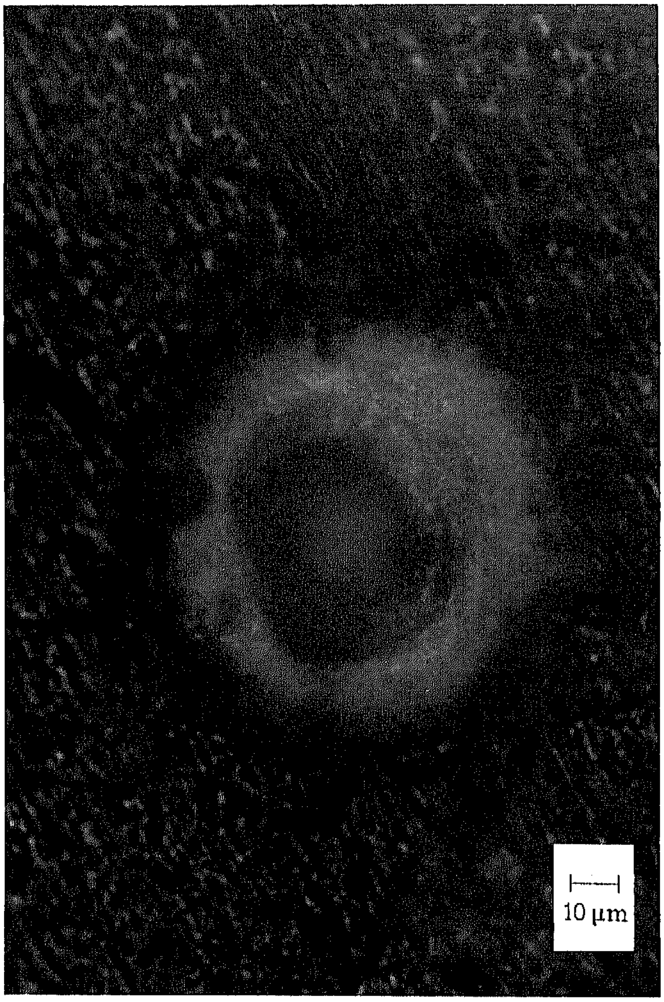

FIG. 7. Optical micrography of a laser-induced crystallized spot on a pellet of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material. Irradiation time of focused (f = 50 mm) laser beam: 0.5 s, laser power: 73 mW, magnification: ×50.

FIG. 8. Scanning electron micrograph of a laser-induced crystallized spot on a pellet of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material. Irradiation time of focused (f = 50 mm) laser beam: 0.5 s, laser power: 445 mW, magnification: ×200.

(arrow) belonging to phase-separated PbO is clearly visible at 144 cm^{-1}. For periods of time longer than about 96 min of heat treatment at 550°C all the Raman modes indicating crystalline perovskite structure are fully developed. The Raman spectrum shown in Fig. 3 for a time period of 192 min is coincident with the spectrum for a related polycrystalline PZT sample reported by Burns and Scott.[5] Our measurements indicate that, despite the homogeneity of the sol-gel derived powders, it takes a certain amount of time before the atoms assume their correct positions in the crystal lattice.

Previous work on PZT pointed out the problem of lead monoxide loss by phase separation;[6-8] diffusion of Pb^{2+} and O^{2-} to the surface is followed by the reaction at or near the surface to form PbO and subsequent vaporization of PbO. It is known that the loss of PbO and the resultant variation in composition affect both the densification process and the intrinsic electromechanical properties of the ceramic. Figure 4 shows the optical micrograph of pure PbO on the surface of a $PbZr_{0.3}Ti_{0.7}O_3$ pellet, which was heat treated at 700°C. The micro-Raman spectrum of this spot is shown in Fig. 5 (spectrum *A*) together with the Raman spectrum of commercially obtainable PbO (spectrum *B*). Comparison of the two spectra reveals that most of the scattering seen in spectrum *A* is due to PbO. This is a further example that shows the benefit of the application of micro-Raman spectroscopy to the study of micro effects on surfaces.

Raman Spectra of Laser-Processed $PbZr_{0.3}Ti_{0.7}O_3$ Gel Powders. Since the beginning of the eighties, laser annealing of semiconductor surfaces has been an active area of research, and Raman spectroscopy has been successfully used to elucidate its dynamics.[9,10] The formation of lead zirconate titanate materials affected by laser energy has already been investigated by Popescu *et al.*[11] The starting material, however, was a mixture of lead titanate ($PbTiO_3$) and lead zirconate ($PbZrO_3$), and the necessary energy was provided by a TEA-CO_2 laser (λ = 10.6 μm). The mixtures were irradiated on an area of 20 mm^2 with 0.5 kW of laser power.

Here, we report on the transformation of amorphous sol-gel derived $PbZr_{0.3}Ti_{0.7}O_3$ powders into the crystalline phase induced by the 514.5-nm radiation of an argon-ion laser. The employed gel powders were heat treated first at 350°C to burn off most of the organic materials and the water. Pressed into pellets, the samples were exposured to the laser beam, which was focused with a lens (focal length: 50 mm, diameter of the focus: 22 μm). Thus, the entire laser power was concentrated on an area of about 380 μm^2 on the surface of the pellet.

In Fig. 6 we show Raman spectra of $PbZr_{0.3}Ti_{0.7}O_3$ materials, which were irradiated with different laser intensities and for different periods of time. After 10 min of

FIG. 9. Scanning electron micrograph of the region **B** of Fig. 8. Irradiation time of focused ($f = 50$ mm) laser beam: 0.5 s, laser power: 445 mW, *magnification:* ×17,000.

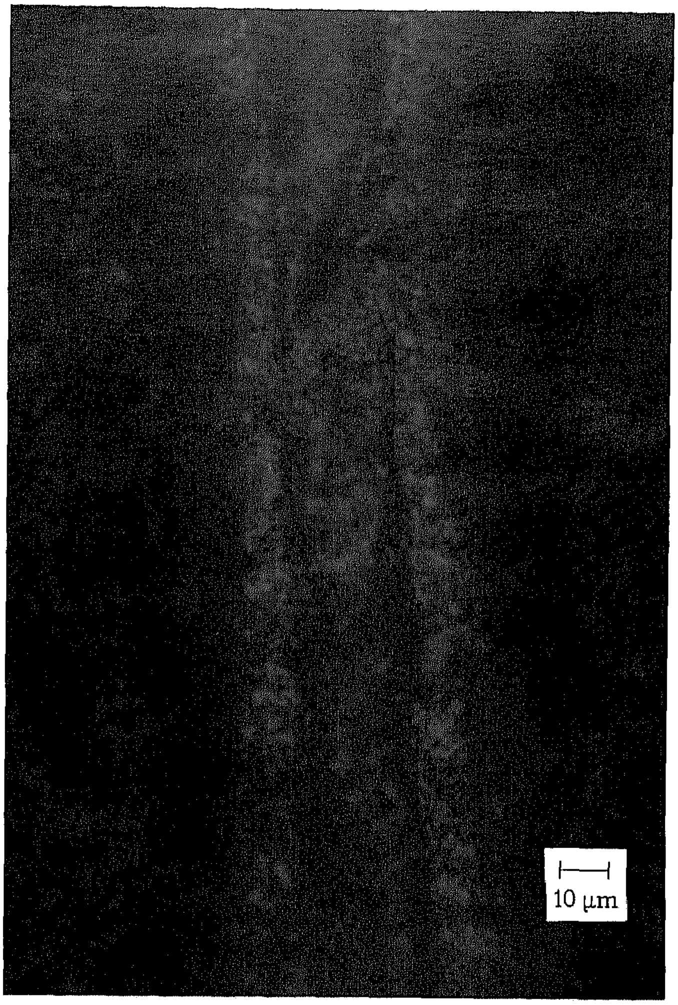

FIG. 10. Optical micrograph of a laser-induced crystallized "trace" on a pellet of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material. Scan rate: 0.5 cm/s, laser power: 73 mW, *magnification:* ×50.

laser annealing at 30 mW, the Raman bands of the perovskite phase are detectable, but they are rather weak, with a relatively low signal-to-noise ratio; and after 20 min of annealing with the same laser power, there is obviously no significant progress in the crystallization process. With 45 mW of laser power the Raman bands get a little more intense, but even after 20 min of irradiation they are still rather weak, indicating that the perovskite structure is not yet well defined.

At a certain laser power, however (depending on the temperature of the previous heat treatment), the transformation of the amorphous to the crystalline state is completed within a fraction of a second (see Fig. 6, upper two spectra). All the features of the perovskite Raman spectrum are fully developed. There are no changes observable in the spectra if higher laser power is applied to the samples for equal duration of time.

Figure 7 shows the optical micrography of a laser-induced crystallized orange-colored spot on a pellet of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material. Because of the Gaussian-shaped laser beam profile, this spot is funnel-shaped. Figure 8 illustrates such a spot by a SEM image with a magnification of 200. Figure 9 is a magnified section of the periphery of the spot center (region **B** of Fig. 8). With a magnification of 17,000 this SEM image shows very well the individual microcrystalline grains and their size distribution.

As is well known, lithography can be performed successfully with the application of lasers. The system discussed above may have some future application in this regard, because of the rapid change from an "amorphous" to a "crystalline" surface under laser irradiation. Figure 10 shows as an example the "trace" of crystalline $PbZr_{0.3}Ti_{0.7}O_3$ on the surface of an amorphous pellet for a scan rate of 0.5 cm/s and argon-ion laser power of only 73 mW.

The Raman spectra from the areas where laser-induced crystallization was achieved revealed no phase-separated PbO. Also, microphotographs did not indicate the occurrence of PbO. Possibly the kinetics of this transformation are too fast, so that the diffusion-controlled process of PbO formation cannot compete. However, to prove this assumption, further work is necessary.

CONCLUSION

Summarizing, we have shown that the phase transformation of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material, prepared by the sol-gel method, into the crystalline perovskite structure can be induced by laser light. Beyond a certain laser power this process shows very quick kinetics, as compared with the experiments of isochronal and isothermal heat treatment of the gel powders in a conventional oven. Besides the x-ray diffraction method, Raman spectroscopy has been shown to be an effective method for these types of investigations. Results of laser treatment of amorphous $PbZr_{0.3}Ti_{0.7}O_3$ material have also been documented by optical and scanning electron micrography. Laser processing can probably provide a new approach to the crystallization and densification processes of PZT ceramics. Additionally, the system discussed may be applicable for lithographic methods. There may be the possibility of enscribing micro-structures onto amorphous PZT surfaces, which could be an interesting technique for the electronics industry.

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