

Review Paper

THIN INORGANIC LAYERS WITH FERROELECTRIC AND FERROMAGNETIC PROPERTIES PREPARED BY THE SOL-GEL METHOD

MIROSLAV SEDLÁŘ, VLASTIMIL MATĚJEC

*Institute of the Chemistry of Glass and Ceramic Materials, Academy of Sciences of the Czech Republic,
Sokolská 38, 120 00 Prague 2*

INTRODUCTION

The sol-gel method is a procedure by which a disarranged infinite network (gel) is formed from a colloidal solution (sol) by the creation of new chemical bonds [1]. The bonds may be formed between molecules, producing so-called polymeric gels, or between particles, yielding so-called colloidal gels. The formation of gels is a complex process, depending primarily on the chemical properties of the precursors and those of the solvent, on the type of catalyst, the pH value, temperature and the way of homogenizing [1]. Although the sol-gel method is widely used in the preparation of glasses, ceramics, thin layers, composites, etc., there is still a number of questions concerning the mechanism of the process which have not so far been answered [2]. There is still little applicable experience (particularly of quantitative character) describing the gelation process, and this restricts effective utilization of the process [3]. The situation can be explained by the complexity of the sol-gel process, and maybe also by the primary goal, which is creation of new materials.

Thin layers (films) of glassy and ceramic materials on various substrates (glass, ceramics, metals, etc.) represent a natural application of the sol-gel method [2]. Its main advantage in the preparation of thin layers is based on a precise control of composition, a high homogeneity and the possibility of coating large areas. Not even the high price of the precursors need be a limiting factor in the preparation of the thin layers.

The preparation of coloured coatings on sheet glass, providing protection from sunlight, and that of reflecting (antireflecting) layers on optical components, were among the first applications of the sol-gel method [2]. Coatings providing chemical protection from alkalis and improving the mechanical strength of the surfaces, or serving as diffusion and oxidation barriers providing protection from high-temperature corrosion, etc., have also been prepared. Thin layers of dielectric materials such as BaTiO₃, PbTiO₃,

Ta₂O₅ etc. have already been utilized in electronic components [5,6]. Electrically conductive layers exhibiting electron conductivity (SnO₂ doped with antimony, Cd₂SnO₄) or ionic conductivity (silicate glasses containing Li₂O) were likewise produced [5].

Spin-coating and dip-coating are the basic methods of preparing thin layers [6]. The former makes often use of standard lithographic machines (e.g. Headway EC101 from Headway Research Inc.), equipped with electronic speed control (50 to 10,000 r.p.m.), automatic cycle control, etc. In the case of dip-coating, creation of the layer results from evaporation of the solvent, gravity-controlled flow of the sol, and hydrolytical and polycondensation reactions [7]. The final layer thickness is given by the concentration of the initial solution, its viscosity, surface tension, the speed of withdrawing (or revolution), temperature and the time of heating the film [7]. Heating up of the gel films results in their drying, sintering and creation of bonds between the base and the film. If these bonding forces are weaker than the cohesive forces inside the film and the heat-treated layer thickness exceeds approx. 0.3 μm, the film would come off the substrate [8]. Thicker films can be prepared by repeating the dipping and the heat treatment of the film.

If ceramic thin layers are to be prepared, gel crystallization has to be brought about. According to crystallization temperature, glasses prepared from gels can be divided into two groups [3]. The boundary between the two groups is given by the temperature corresponding to one half of the melting temperature. A similar classification can also be introduced for glasses prepared from melts [3]. The rate of nucleation and crystallization is higher with glasses prepared from gels than with those prepared from melts [9]. The sol-gel method is suitable for producing ceramic films with preferential crystal orientation [49–51]. The method is also convenient for the preparation of transparent crystalline layers [54].

The present article deals with the possibilities of

the sol-gel method for preparing thin layers with ferroelectric and ferromagnetic properties. The conditions of their preparation, their properties and their application in the form of films on substrates of both planar and cylindrical geometry are described.

FERROELECTRIC THIN LAYERS

Dielectric and electrooptical properties of ferroelectric thin layers provide conditions for their application in electronics and optoelectronics. Films were already prepared of BaTiO_3 , PbTiO_3 , $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), LiNbO_3 , $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN), $\text{Pb}_{1-y}\text{La}_y(\text{Zr}_x\text{Ti}_{1-x})_{1-y/4}\text{O}_3$ (PLZT) and $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ (SBN).

The properties of ferroelectric ceramics depend on the conditions existing at the boundaries of the individual grains [13]. This is why the process parameters (temperature, concentration, the water to alkoxide molar ration, viscosity, sol pH and others) will have a substantial effect on the formation and development of crystallographic phases, the development of microstructure and the final properties of the material [1, 12–17].

In the case of ferroelectric thin layers, the polymer gel is generally prepared from the precursor alkoxides, or from a mixture of a network forming alkoxide, acetates, hydroxides, etc. In this way, thin films of BaTiO_3 were prepared [19–22]. In producing BaTiO_3 films (0.2–0.3 μm), Muralidhar [22] used higher Ti and Ba alkoxides dispersed in xylene. He found that thermally stable BaCO_3 reacted with TiO_2 only as at high as about 650°C. Dosch [21] prepared BaTiO_3 films (0.1–0.3 μm) on Si, Ti and Ni carriers from solutions of Ti isopropoxide and $\text{Ba}(\text{OH})_2$ in methanol.

The problem of increasing the thickness of thin ferroelectric layers by a single process step was also studied. Sayer [10], using the spin-coating method, obtained PZT films about 1 μm in thickness. He used lead acetate trihydrate, zirconium *n*-propoxide and titanium isopropoxide in propanol with ethylene glycol as precursors in sol preparation. By replacing 2-methoxyethanol as solvent for ethylene glycol, Phillips [11] prepared PbTiO_3 films 1 μm in thickness by dip-coating. Pyke [18] used acetyl acetonates in place of alkoxides to prepare PbTiO_3 and PZT films. By the dip-coating method he obtained films 1 μm thick by one process step.

Sayer [24] prepared PLZT thin films (0.3–0.8 μm) and studied their dielectric properties. The precursor sol was obtained from titanium and zirconium propoxides, lead and lanthanum acetates and 2-methoxy ethanol as a solvent. The lower solubility of lanthanum acetate (about 10 mol.%) is adequate for current compositions of PLZT ceramics. The results showed that adhesion of the ferroelectric film to

the substrate is decisive for the final properties [10, 24]. The adhesion can be improved by using a conductive oxidic material as contact electrode. The adhesion was increased by applying a PLZT film onto SnO_2 with an addition of indium (ITO), [24]. However, during heat treatment of the ferroelectric film, the processes taking place at the PLZT- SnO_2 boundary may affect negatively the final properties, where both the diffusion of Pb and formation of the non-ferroelectric PbO phase at the PLZT- SnO_2 boundary increase the coercive force E_c (about 300 kV/cm compared to 30 kV/cm for PZT [10], as well as the dielectric losses. The ferroelectric properties of the film prepared in this way, which are a function of its thickness and annealing temperature, are plotted in Fig. 1 a, b.

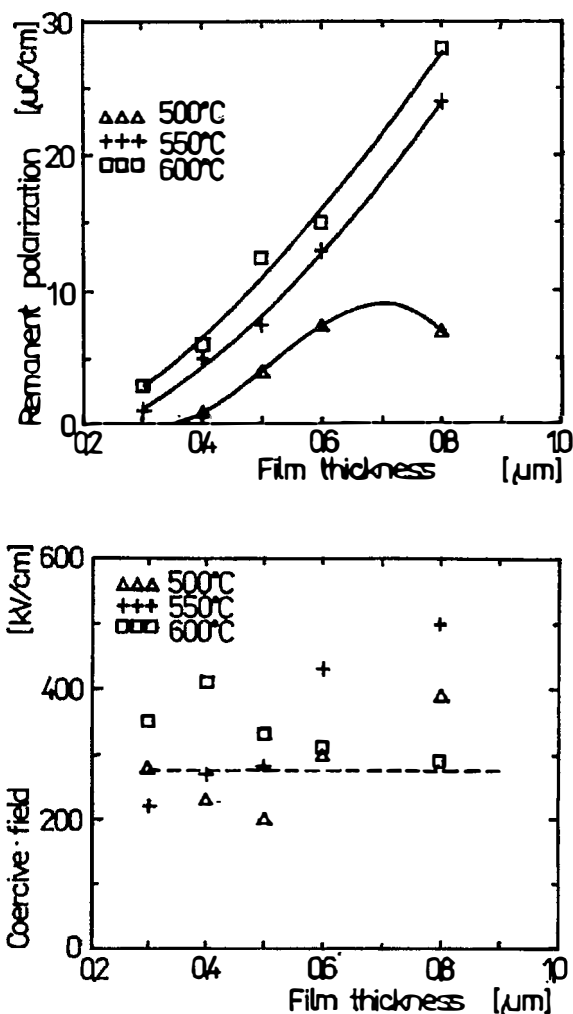


Fig. 1. Remanent polarization (a) and coercive force (b) vs. the thickness of PLZT film for various firing temperatures.

Table I

Relative permittivity of ferroelectric films prepared by the sol-gel method

Material	Composition	Rel. permittivity	Reference
PZT	$x = 0.6$	289 on ITO at 100 kHz	[10]
	$x = 0.44$	1200 on Pt up to 10 MHz	[25]
	$x = 0.52$	620 on Pt at 1 kHz	[63]
PZT	amorphous	50-60 on Pt	[25]
PLZT	$x = 0.65, y = 0.07$	130 on Si at 100 kHz	[62]
		225 on Au at 100 kHz	[62]
PFN		2000 at 60 kHz	[52]
Ta ₂ O ₅		20 at 1 MHz	[53]

Temperature: 25°C

Table II

Electrooptical coefficients and electromechanical coupling coefficients

Linear electrooptical coefficient r_c (m/V)		electromechanical coupling coefficient	
PZT [†] ($x = 0.6$)	2.5×10^{-11}	PZT* ($x = 0.55$)	0.4
PLZT* ($y = 0.08, x = 0.65$)	61.2×10^{-11}	PLZT*	0.65
PbTiO ₃ [†]	0.79×10^{-11}		

[†] ... film, prepared by the sol-gel method [10]

* ... monolithic material of powder oxides [33]

In preparing thin layers of LiNbO₃ (0.1–0.3 μm), Partlow [34] used a sol containing LiOCH₃ and Nb(OC₂H₅)₅ in dry ethanol. It was found that if a stable sol is to be obtained, the water/alkoxide molar ratio R_w has to be reduced to obtain higher alkoxide concentrations. This in turn results in a greater layer porosity. The film microstructure was also influenced by the heat treatment conditions (435°C, 30 minutes – amorphous films, 500–800°C, 2 hours – the films contained microcrystals 0.2–0.5 μm in size).

Chen and Ryder [13] prepared PbTiO₃ films (0.1–0.5 μm) by spin-coating (the precursor sol was obtained from titanium isopropoxide and lead acetate in 2-methoxyethanol). They studied the effect of the substrate on the macrostructure of the films. Whereas on alumina and fused quartz the film structure was random-oriented, thin layers with a distinct structural orientation in the 100 direction were obtained on MgO monocrystals, and the orientation increased with decreasing film thickness and decreasing

water/alkoxide ratio in the precursor mixture. Thin films of LiNbO₃ with preferential orientation were prepared on sapphire (crystallization temperature 400°C), [49], Li₂B₄O₇ layers on quartz and sapphire monocrystals [51] and perovskite PMN layers on Pt and MgO monocrystal [50].

The relative permittivity values of ferroelectric films range from 10² to 2 × 10³, depending on frequency, type of substrate, the film structure, its composition and the temperature of measurement (Table I). Ferroelectrics of the PZT and PLZT types, compared to PFN ferroelectrics, show lower values of relative permittivity. On the contrary, as compared to Ta₂O₅, with which no hysteresis was established, the values of relative permittivity are higher for the PZT ceramics. Type PZT and PLZT ceramics exhibit higher Curie temperatures (about 500°C), lower coercive force values, and attain very satisfactory piezoelectric and electrooptical properties (Table II).

Compared to monoliths, ferroelectric thin films as

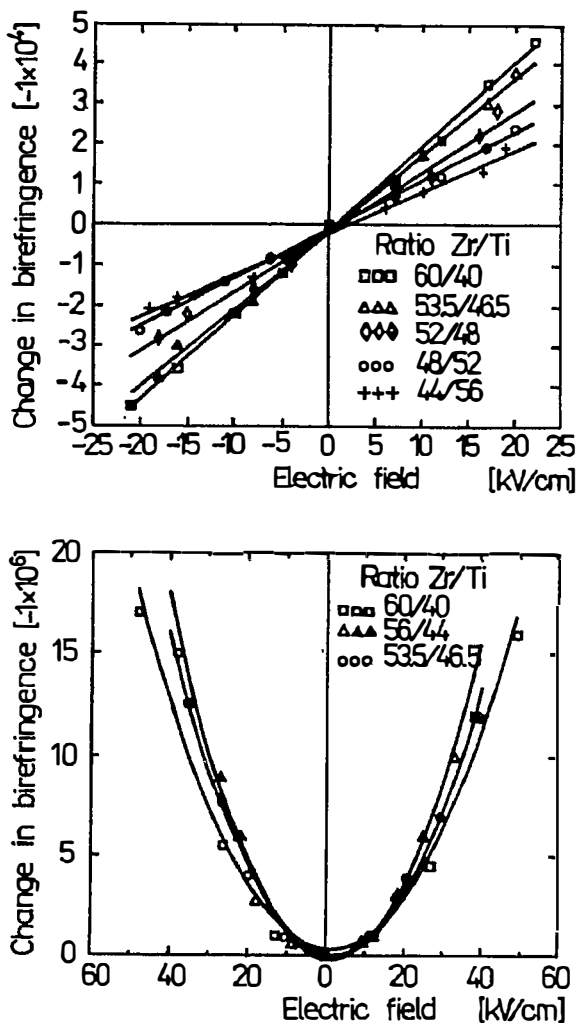


Fig. 2. Birefringence vs. electric field intensity for PZT films with various Zr/Ti ratios, with poling (a) and without poling (b).

a rule exhibit lower values of remanent polarization and higher values of coercive force, which may be explained by the formation of smaller grains in these films, as well as by the difference in the expansion coefficients of the substrate and the film [27].

Banno [16] has theoretically derived and experimentally proved that the ferroelectric properties depend not only on the volume share of pores in the ceramic material, but also on their shape and distribution. However, they do not depend on their size. In the case of PZT crystals prepared by Sayer [10], which were poled (electric field intensity $E = 31 \text{ kV/cm}$, temperature 200°C) for a period of 20 to 100 minutes, the linear and electrooptical phenomena were measured (Fig. 2a); a solely quadratic electrooptical phenomenon was established on the non-poled films (Fig. 2b).

Xu and Mackenzie [54] prepared a transparent SBN ferroelectric film with preferred crystalline orientation on silica glass. They found that Kerr's phenomenon occurs in this layer. Satisfactory electrooptical properties are likewise showed by LiNbO_3 [34, 60].

PZT ceramics in the form of thin films were also applied by the sol-gel method onto substrates of cylindrical geometry (optical fibres, alumel wire, etc.). Electroacoustic transducers and special elements for optical fibre technology (lens for acoustic microscopy and phase or frequency modulators) were constructed on this principle [35–42]. The fibre transducers can be operated even at frequencies higher than 500 MHz (with monolithic PZT transducers the maximum frequency amounts to about 150 MHz). Sayer [38], using a procedure described in [10], prepared a lens for acoustic microscopy by applying a PZT film ($7 \mu\text{m}$) onto a quartz cylinder (Fig. 3). Its function was verified by making an acoustic micrograph of a calibration grid.

An optical fibre phase modulator was prepared by repeated dipping of an optical fibre in PZT sol [10], heating the layer (500°C , 12 hours) and poling it (175°C , 30 kV/cm , 2 hours) [37, 38]. On connecting an alternating electric field at frequencies from 1 Hz to 10 kHz to the PZT film, one can modulate the signal passing through the fibre. The modulation is caused by mechanical vibrations of the fibre due to piezoelectric properties of the PZT film. In addition to the function of modulators, electrically controlled deviation of a beam (e.g. a laser one) passing through the fibre could be utilized in medicine [36, 37].

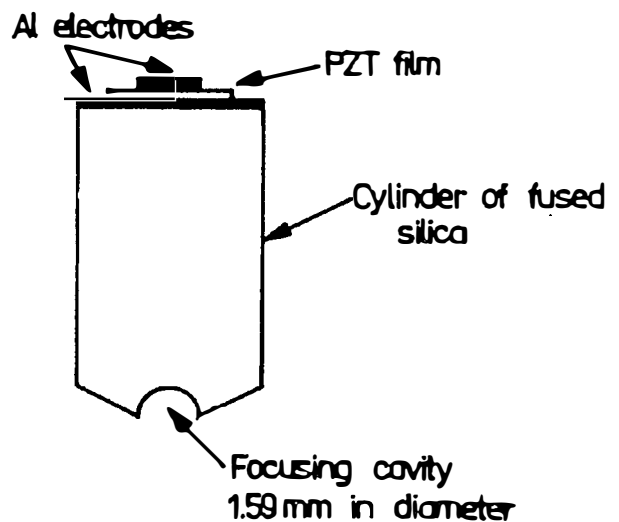


Fig. 3. Schematic diagram of an acoustic microscopic lens.

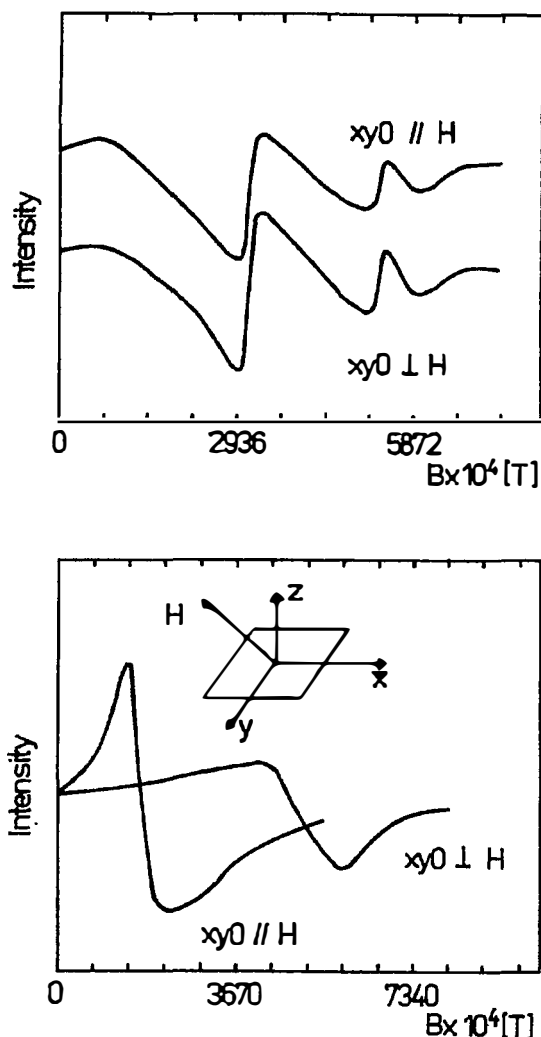


Fig. 4. ESR spectrum of iron oxides placed parallel with, and perpendicularly to, the magnetic field before (a) and after (b) heat treatment in H_2 atmosphere at $620^\circ C$.

The studies described in the paragraphs above indicate the possibility of creating new optical sensors by preparing ceramic thin films on optical fibres. Under the effect of outer force fields on a standard optical fibre, the phase shifts described are generally small. The sensitivity to these fields can be increased by up to several orders by coating the fibre with a suitable layer [56]. Hocker [57] dealt in detail with an analysis of elasticity of such composite structures from the standpoint of acoustic sensitivity. The effect of outer magnetic field on optical fibre with metallic magnetostrictive coatings was studied theoretically [58]. The possibility of measuring the intensity of an outer electric field by means of an optical fibre attached to a piezoelectric base of polyvinylidene fluoride was also examined (the sensitivity attained was about $E = 33 \mu V/m$ per 1 m of fibre [59]). A fibre coated with PZT

film may also be utilized in sensors reacting to outer electric fields.

Thin films of ferroelectric materials, prepared by the sol-gel method, have already been utilized in electrooptical instruments, in the design of electromechanical transducers and in that of non-volatile memory media [23–28].

FERROMAGNETIC THIN LAYERS

Thin magnetic films of $Fe^{II}Fe_2^{III}O_4$ were among the first to be prepared using the dip-coating method and borosilicate glasses as a substrate [45]. The magnetic properties depended on the conditions of heat treatment. Following heating the film in H_2 atmosphere ($620^\circ C$, 2 hours), the layer was magnetically anisotropic (Fig. 4b). If not treated in this way, it was magnetically isotropic (measured by the method of electron spin resonance (ESR), Fig. 4a).

Thin layers ($0.05\text{--}0.3 \mu m$) containing for the most part finely dispersed particles of $\gamma\text{-}Fe_2O_3$, were prepared by applying the sol of $(Fe(NO_3)_3)$ in ethylene glycol at 15 wt.% concentration by spin-coating onto carriers of borosilicate glass in study [61]. As the $\gamma\text{-}Fe_2O_3$ particles did not show any structural magnetic anisotropy, very low values of coercive force of the film were measured (max. 1.989 kA/m (250 Oe)). The saturated magnetization was increasing with increasing calcination temperature up to $0.052 \text{ Am}^2\text{g}^{-1}$ (52 emu/g) at $450^\circ C$. With $\gamma\text{-}Fe_2O_3$ one can observe a distinct Faraday's effect $\Theta_F = -2.2 \times 10^4 \text{ deg/cm}$ at $\lambda = 442 \text{ nm}$). This is why the films could be utilized as media for magneto-optical recording [61] if the value of the coercive force can be increased.

Magnetic properties are likewise exhibited by systems containing the rare earth elements (e.g. those with Pr, Nd, Tm, Eu, Gd, Ho and Er [46]). No thin layers of this system have yet been prepared by the sol-gel method. The magnetic properties were only measured on monolithic samples of silicate glasses containing the elements Pr, Dy and Er. Magnetic susceptibility measurements showed that no ferromagnetic structure of the domain type was formed in the glasses [47].

Hexagonal ferrites of the type $MO.6Fe_2O_3$, where M^{II} is Ba, Sr or Pb, exhibit high values of the coercive force. The magnetic anisotropy of hexagonal ferrite can be suppressed by suitable substitution for Fe^{III} ions. For example, Tsuchiya [48] prepared by dip-coating a ferrite having the composition

$$y.MO.(100 - y).[(100 - 2x)Fe_2O_3.xCoO.xTiO_2],$$

where $M = \text{Ba or Sr}$, $y = 0\text{--}25$ and $x = 0\text{--}11.66$. The precursor sol, which contained nitrates of the metals and titanium oxoacetyl acetonate $(TiO_2(C_5O_2H_7)_2)$ in a mixture of water, glycerine and formamide, was applied onto quartz substrates. Multiple applications

yielded films about $0.3 \mu\text{m}$ in thickness. The crystalline phase of magnetoplumbite type began to form during heat treatment at 750°C . Substitution with Co and Ti ions resulted in a reduction of the coercive force by an order of magnitude (Fig. 5a). Substitution was responsible for increasing saturated magnetization for composition $x < 8.33$ (Fig. 5b).

Tsuchiya [55] prepared thin films of ferrite ($0.2 \mu\text{m}$) having the composition $\text{Y}_{3-x}\text{Bi}_x\text{Fe}_5\text{O}_{12}$ ($x = 0.4-1$) from nitrates of the respective metals in ethylene glycol as solvent. The films showed an optical permeability of about 80% over the 500–700 nm region, and a saturated magnetization of $0.08 \text{ Am}^2\text{g}^{-1}$ (80 emu/g).

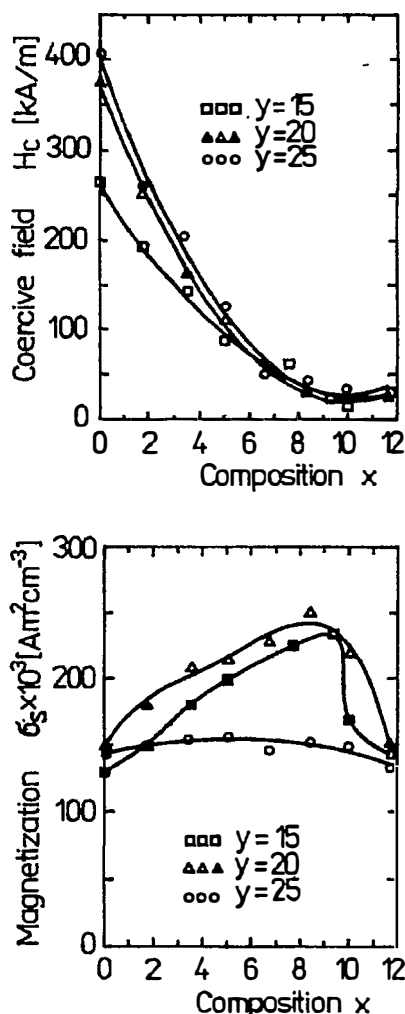


Fig. 5. Substitution effect of titanium and cobalt on the coercive force (a) and saturated magnetization (b) of films in the system having the composition $y.\text{MO} \cdot (100 - y) \cdot [(100 - 2x) \cdot \text{Fe}_2\text{O}_3 \cdot x \text{CoO} \cdot x \text{TiO}_2]$, heat treated at 820°C for 48 hours.

CONCLUSION

On the basis of the information summarized above, certain conclusions can be drawn from the standpoint of preparation of thin layers by the sol-gel method. In the case of ferroelectric ceramic films, research in the sol-gel field is not concentrated on seeking quite new materials. The attention is rather more paid to studying the conditions for preparing the given material and improving its final parameters, to investigating the effects and geometry and properties of the base, and its interaction with the thin layer applied. The transition to ferroelectric materials in the form of thin layers has allowed the frequency of acoustic transducers to be increased.

With ferromagnetic thin layers, research is concentrated primarily on new types of ferrite showing reduced anisotropy and coercive field forces (particularly substituted hexagonal ferrites for magnetic recording in the perpendicular direction [48, 64], and on studying the conditions for their preparation by the sol-gel method.

A new direction of research may be the study of dielectric material structures represented by a cylindrical base and a thin film with ferroelectric or ferromagnetic properties. These structures may find application in the design of new optical fibre sensors, as well as in new elements for electronics and optoelectronics.

References

- [1] Schmidt H.: *J. Non-Cryst. Solids* **100**, 51–64 (1988).
- [2] Uhlmann D.R., Zelinski B.J.J., Wrek G.E.: *Better Ceramics Through Chemistry*, ed. by Brinker C.J., Clark D.E., Ulrich D.R., **32**, 59 (1984).
- [3] Mackenzie J.C.: *N. Non-Cryst. Solids* **100**, 162–168 (1988).
- [4] Wachtman J.B., Sheppard L.M.: *Ceram. Bull.* **63**, 91–95 (1985).
- [5] Yoko T., Kamiya K., Sakka S.: *Research Report Fac. Eng. Mie Univ.* **12**, 49–64 (1987).
- [6] Sakka S.: *Sol-Gel Science and Technology*, World Scientific, Singapore, 346 (1989).
- [7] Brinker C.J., Hurd A.J., Frye G.C., Ward K.J., Ashley C.S.: *J. Non-Cryst. Solids* **121**, 294 (1990).
- [8] Sakka S.: *J. Non-Cryst. Solids* **63**, 223–235 (1984).
- [9] Mukherjee P., Zarzycki J., Traverse J.P.: *J. Mat. Sci.* **11**, 341–355 (1976).
- [10] Yi G., Wu Z., Sayer M.: *J. Appl. Phys.* **64**, 2717 (1988).
- [11] Phillips N.J., Milne S.J.: *Proc. of Abstracts of 6th International Workshop on Glasses and Ceramics from Gels*, B04, Seville, Spain (1991).
- [12] Scherer G.W.: *J. Non-Cryst. Solids* **100**, 77–92 (1988).
- [13] Chen Ch., Ryder F.D.: *J. Am. Ceram. Soc.* **72**, 1495–1498 (1989).
- [14] Selmi F.A.: *J. Am. Ceram. Soc.* **71**, 934 (1988).

- [15] Budd K.D., Dey S.K., Payne D.A.: *Br. Ceram. Proc.* **36**, 107–121 (1985).
- [16] Banno H.: *Ceram. Bull.* **66**, 1332 (1987).
- [17] James P.F.: *J. Non-Cryst. Solids* **100**, 93–114 (1988).
- [18] Pyke S., Milne S.J.: *Proc. of Abstracts of 6 th International Workshop on Glasses and Ceramics from Gels*, CP39, Seville, Spain (1991).
- [19] Fukushima J.: *Yogyo-Kyokai-Shi* **83**, 204 (1975).
- [20] Goosey M.T., Patel A., Watson I.M., Whatmore R.W.: *Br. Ceram. Proc. No.41*, 49–58 (1989).
- [21] Dosch R.G. in *Better Ceramics Through Chemistry*, ed. by Brinker C.J., Clark D.E., Ulrich D.R., **32**, 157 (1984).
- [22] Muralidhar S.K., West R.V.: *American Ceramic Society 86-th Annual Meeting, Pittsburgh, USA, May 1984*, in *Am. Ceram. Soc. Bull.* **63**, No.4, p. 486 (1984).
- [23] Quek H.M., Yan M.F.: *Ferroelectrics* **74**, 95–108 (1987).
- [24] Wu Z., Sayer M.: *Interní zpráva*, 1990
- [25] Dey S.K., Zuleeg R.: *Proceedings of the '1 st Symposium on Integrated Ferroelectrics', Colorado Microelectronics Conference, March 30–31, (1989)*.
- [26] Scott J.F. et al.: *J. Appl. Phys.* **64**, 787–92 (1988).
- [27] Chen C.J., Wu E.T., Xu Y.H., Chen K.C., Mackenzie, J.D.: *Ferroelectrics* **112**, 321–327 (1990).
- [28] Melnick B.M., Cuchiaro J.D., McMillian L.D., Dearaujo C.A.P., Scott J.F.: *Ferroelectrics* **112**, 329–351 (1990).
- [29] Kato I.: *Ceram. Eng. Sci. Proc.* **8**, 1120 (1987).
- [30] Kato I., Gonzales-Oliver C.J.R.: *J. Non-Cryst. Solids* **82**, 400 (1988).
- [31] Klein L.: *Sol-gel Technol. for Thin Films, Fibres, Preforms, Electronics and Specially Shapes*, ed. by Noyes Publication (1988).
- [32] Arfsten N.J., Kaufmann R., Dislich H.: *Ultrastructure Processing of Ceramics, Glasses and Composites*, 189–196, New York (1984).
- [33] Haertling G.H., Land C.E.: *J. Am. Ceram. Soc.* **54**, 1 (1971).
- [34] Partlow P.D., Gregg J.: *J. Mat. Res.* **2**, 595 1(1987).
- [35] Yi G., Sayer M., Wu Z.: *Electron. Lett.* **25**, 907 (1987).
- [36] Sayer M. et al.: *Proc. IEEE, Ultrasonic Symposium*, 1231 (1989).
- [37] Wu Z., Sayer M., Jen C.K.: *Proc. IEEE, Ultrasonic Symposium*, 653 (1989).
- [38] Sayer M., Yi G., Jen C.K., Neron C., Cheeke D.N.: *Materials Science and Engineering A122*, 21 (1989).
- [39] Engan, H.E., Myrtrveit, T., Askautrud, J.O.: *Optics Letters* **16**, 1 (1991).
- [40] Depaula R.P., Moore E.L.: *SPIE* **478**, 3–11 (1984).
- [41] Taylor H.F.: *IEEE J. of Lightwave Technol.* **LT-5**, 990 (1987).
- [42] Heffner B.L., Risk W.P., Khuri-Yakub B.T., Kino G.S.: *Proc. IEEE Ultrasonics Symp.*, 715 (1986).
- [43] Jen C.K., Neron C., Yi G., Sayer M.: *Materials Sci and Eng. A122*, 25 (1989).
- [44] Oda K., Yoshio T.: *J. Mat. Sci. Lett.* **5**, 545 (1986).
- [45] Kordas G., Weeks R.A., Arfsten N.: *J. Appl. Phys.* **57**, part 28, 3812 (1985).
- [46] Smit J., Wijn H.P.J.: *Ferrites*, Eindhoven, Holland (1959).
- [47] Sun K., Lee W.H., Risen W.M.: *J. Non-Cryst. Solids* **92**, 145–152 (1987).
- [48] Tsuchiya T., Yamashiro K., Mackenzie J.D.: *J. Ceram. Soc. Jpn. Inter. Ed.* **97**, 903–909 (1989).
- [49] Hirano S., Kato K.: *Adv. Ceram. Mater.* **3**, 503 (1988).
- [50] Okuwada K., Imai M., Kakuno K.: *Jpn. J. Appl. Phys.* **28**, L1271 (1990).
- [51] Yamashita H., Yoko T., Sakka S.: *J. Ceram. Soc. Jpn.* **98**, 913 (1990).
- [52] Kamg J., Yoko T., Sakka S.: *zasláno do J. Am. Ceram. Soc.*
- [53] Silveraman L.A., Teowee G., Uhlmann D.R.: *Mat. Res. Soc. Symp. Proc.* **73**, 725 (1986).
- [54] Xu Y., Chen C.J., Mackenzie, J.D.: *Proc. SPIE 1990 Symp.* 1328 (1990).
- [55] Tsuchiya T., Sei T., Kanda H.: *Proc. of Abstracts of 6 th International Workshop on Glasses and Ceramics from Gels*, C05, Seville, Spain (1991).
- [56] Harmer A.L.: *Čs. čas. pro fyziku A36*, 1–96 (1986).
- [57] Hocker G.B.: *Appl. Optics* **18**, 3679 (1979).
- [58] Jarzynski J., Cole J.H., Bucaro J.A., Davis C.M.: *Appl. Optics* **22**, 3746 (1980).
- [59] Koo K.P., Sigel G.H.: *IEEE J. Quant. Elect.* **QE-18**, 670 (1982).
- [60] Nashimoto, K., Cima, M.J.: *Materials Letters* **10**, 348–354 (1991).
- [61] Takahashi N. et al.: *J. Mat. Sci.* **26**, 497 (1991).
- [62] Seth K.V., Schulze W.A.: *Ferroelectrics* **112**, 283–307 (1990).
- [63] Tohde N., Takahashi S., Minami T.: *J. Am. Ceram. Soc.* **74**, 67–71 (1991).
- [64] Görnet P., Sinn E., Schüpel W., Pfeiffer H.: *IEEE Transactions on Magnetics*, **26**, No.1, 12 (1990).

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