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Preparation and properties of mixed La–Pr silicate oxynitride glasses

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ABSTRACT

The preparation and properties of mixed lanthanide (La, Pr) silicate oxynitride glasses are reported. These oxynitride glasses were prepared by melting mixtures of La, Pr, SiO_2 and Si_3N_4 powders in a nitrogen atmosphere at 1750 °C. The glasses were characterized by X-ray powder diffraction, differential thermal analysis, scanning and transmission electron microscopy. Glass compositions were calculated from the analyses obtained by energy dispersive X-ray (EDX) spectroscopy and combustion analysis, for cation and anion compositions, respectively. The glasses were found to be homogenous, optically opaque black, and to contain contents up to 66 e/o of N and up to 48 e/o of La–Pr. The physical properties were found to vary linearly with the degree of substitution of La by the Pr. Determined glass density increases substantially upon the substitution of La by Pr, up to 5.49 g/cm^3. The calculated molar volumes and compactness values decrease and increase respectively by the substitution of Pr for La. Glass transition temperatures and microhardness increase upon the substitution by Pr, up to 1086 °C and 10.98 GPa, respectively. The refractive index increases upon the substitution by Pr up to 2.00.

1. Introduction

The incorporation of nitrogen atoms into oxide glass networks of e.g. silicates, borates and phosphates creates the materials known as oxynitride glasses [1–3]. The majority of studied oxynitride glasses are silicate based glasses, which often also contain Al or, less frequently, B. The term oxynitride glass is thus often used synonymously to mean oxynitride silicate glass. Silicon oxynitride glasses have received considerable special scientific and technological attention, since the late 70s due to their superior properties compared to their oxide counterparts. Recent studies have shown that M–Si–O–N (M = La–Mg–Ca–Sr–Ba) glasses can be formed over wide compositional ranges by using the electropositive elements in their metallic or metallic hydride state as starting materials. These glasses retain high amounts of the electropositive elements and nitrogen during formation and therefore they exhibit higher values of glass transition temperature, microhardness and refractive index compared to analogue oxide glasses [4–7]. The present La–Pr–Si–O–N glasses were prepared by using this synthesis approach.

For oxynitride glasses with rare-earth (RE) or alkali earth (AE) elements, studies [8–14] have shown that changes in molar volume (MV), hardness, elastic properties and glass transition temperature (T_g) are controlled by the cation field strength (CFS) of the modifier or an effective CFS in the case of a mixed modifier glass. It is, however, clear, as shown by e.g. the study by Becher et al. [9], that the Young's modulus and microhardness of RE–Si–Al–O–N glasses (RE = La, Nd, Gd, Y, Lu) not only depend on the type of RE element but also on the amounts of RE and nitrogen.

Studies of mixed modifier containing (RE/AE) oxynitride glasses are up till now few and these have been directed at the effects of nitrogen substitution for oxygen rather than the effect of mixed cation modifier ratios [15,16]. An exception is the study by Pomeroy et al. [8] and Sharafat et al. [17] on the properties of RE glasses and AE glasses respectively with mixed modifiers and constant Si:(Al):O:N ratios. In the current study, the preparation and properties of silicon oxynitride glasses with mixed RE (La–Pr) modifiers were evaluated. The nominal pure La glass composition was chosen as $La_{12.46}Si_{10}O_{13.15}N_{17.03}$ (containing 48 eq.% or e/o La and 66 e/o N), denoted 1 (*c.f.* Table 1). The substitution limit of La by Pr was determined, as well as the effect of Pr content on properties such as density, molar volume, glass compactness, glass transition and crystallization temperatures, hardness and refractive was investigated.

2. Experimental

Starting compositions for melting experiments were prepared by thoroughly mixing weighed amounts of La and Pr metals (ChemPur GmbH), SiO_2 (Silicon (iv) oxide 99.9%, ABCR GmbH & Co.), and Si_3N_4 (UBE, SNE10) powders. The powders were weighed inside the glove box and then pressed into pellets. Syntheses were performed in an atmosphere of nitrogen gas, serving as a nitridation source for metals. The mixtures were melted in Nb crucibles at 1750 °C, using a radio frequency furnace. The samples were heated up to 900 °C during 15 min and held at this temperature for 30 min. Then samples were heated to

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Table 1
Data for prepared La–Pr–Si–O–N glasses; composition of starting mixture, determined glass composition, La content in eq.%, Pr content in eq.%, La + Pr contents in eq.%, O content in eq.% and N content in eq.%.

ID	Nominal composition	Glass composition	La eq.%	Pr eq.%	Si eq.%	La + Pr eq.%	O eq.%	N eq.%
1	$La_8Si_{10}O_8N_{16}$	$La_{12.46}Si_{10}O_{13.15}N_{17.03}$	48.31	0	51.69	48.32	33.98	66.01
2	$La_{7.84}Pr_{0.16}Si_{10}O_8N_{16}$	$La_{13.92}Pr_{0.42}Si_{10}O_{14.40}N_{18.07}$	50.30	1.52	48.18	51.81	34.70	65.30
3	$La_{7.6}Pr_{0.4}Si_{10}O_8N_{16}$	$La_{12.55}Pr_{0.78}Si_{10}O_{15.43}N_{16.38}$	47.07	2.92	50.01	50.00	38.58	61.42
4	$La_{7.2}Pr_{0.8}Si_{10}O_8N_{16}$	$La_{11.84}Pr_{1.28}Si_{10}O_{16.40}N_{15.52}$	44.76	4.83	50.40	49.59	41.33	58.66
5	$La_{6.4}Pr_{1.6}Si_{10}O_8N_{16}$	$La_{11.31}Pr_{2.41}Si_{10}O_{15.34}N_{16.83}$	41.81	8.91	49.29	50.71	37.80	62.21
6	$La_{5.6}Pr_{2.4}Si_{10}O_8N_{16}$	$La_{10.09}Pr_{4.04}Si_{10}O_{14.96}N_{17.49}$	36.74	14.71	48.55	51.45	36.32	63.68
7	$La_{4.8}Pr_{3.2}Si_{10}O_8N_{16}$	$La_{8.55}Pr_{5.41}Si_{10}O_{16.08}N_{16.58}$	31.33	19.82	48.85	51.15	39.27	60.73
8	$La_4Pr_4Si_{10}O_8N_{16}$	$La_{6.63}Pr_{6.38}Si_{10}O_{16.07}N_{15.63}$	25.17	24.22	50.61	49.38	40.67	59.33
9	$La_{3.2}Pr_{4.8}Si_{10}O_8N_{16}$	$La_{4.81}Pr_{7.35}Si_{10}O_{15.25}N_{15.32}$	18.87	28.83	52.30	47.68	39.89	60.11
10	$La_{2.4}Pr_{5.6}Si_{10}O_8N_{16}$	$La_{4.77}Pr_{10.2}Si_{10}O_{15.83}N_{17.75}$	16.85	36.04	47.11	52.90	37.29	62.71
11	$La_{1.6}Pr_{6.4}Si_{10}O_8N_{16}$	$La_{3.01}Pr_{11.04}Si_{10}O_{16.26}N_{16.55}$	10.99	40.32	48.69	51.31	39.58	60.42
12	$La_{0.8}Pr_{7.2}Si_{10}O_8N_{16}$	$La_{1.52}Pr_{11.49}Si_{10}O_{15.66}N_{15.90}$	5.77	43.62	50.61	49.39	39.64	60.36
13	$Pr_8Si_{10}O_8N_{16}$	$Pr_{12.65}Si_{10}O_{15.96}N_{15.35}$	0	48.69	51.31	48.69	40.94	59.06

1200 °C during 15 min and held at this temperature for 30 min, for a complete reaction of the metals with nitrogen gas, and then finally heated up to 1750 °C during 1 to 2 h, depending on the composition. The melts were cooled by turning off the furnace at the end of the run. The glasses were quenched in such a manner as to avoid the build-up of internal stresses during cooling. The samples were quenched from 1750 to 900 °C in 5 min, then from 900 to 500 °C in 30 min, and then further down to room temperature in 1 to at the most 2 h under a flow of nitrogen gas.

The amorphousness of the glasses was verified by powder X-ray diffraction, using a Panalytical X'pert PRO MPD diffractometer and CuKα_1 radiation. The chemical homogeneity of the glasses was examined by back-scattered electron images using a JSM 7000F scanning electron microscope. Cation concentrations were determined by energy dispersive X-ray (EDX) point analysis, 20 on each sample, on polished and carbon-coated surfaces, using LINK INCA program system. Oxygen and nitrogen contents were determined by combustion analysis using LECO equipment. For transmission electron microscopy (TEM) observations, foils/crushed samples were examined by electron energy-loss spectroscopy, using a scanning transmission electron microscope VG HB501 UX with a cold field emission gun and an electron energy-loss spectrometer, Gatan Enfina 1000, attached in parallel. High resolution TEM (HRTEM) studies were done with a Jeol H-8100 (200 keV, EDXS) and JEM 3010 and 4010 (400 keV) microscopes.

Densities were determined accordingly by the Archimedes method. Glass transition temperature and crystallization temperature were measured on crushed pieces of glass, placed in Pt cups, using differential thermal analysis (DTA) up to 1400 °C in flowing nitrogen with a NETZSCH STA 409PC instrument. Vickers hardness (at 500 g) values were measured using a Matsuzawa microhardness tester, Model MXT-a 1 (Akita, Japan), with a pyramid-shaped diamond indenter. The Refractive index (at 640 nm) was estimated by measuring the Brewster's angle θ_B, further details regarding the physical properties measurement are described in Ref. [5–7]. Molar volume and glass compactness values were calculated according to the equation given in Ref. [1].

3. Results

3.1. Glass formation

Hakeem et al. reported details on the glass forming region of the La–Si–O–N system [7]. In order to study the substitution effect of Pr for La ions in the nominal pure La glass composition, $La_8Si_{10}O_8N_{16}$ having high amount of La 48 e/o and of N 66 e/o was chosen. The limit for the formation of mixed Pr–La glasses was determined and the results showed that all La can be substituted by Pr as shown in Table 1. All obtained glasses were examined by XRPD in order to confirm their amorphous nature which is given in Fig. 1. The glasses were inspected visually by optical microscopy at 100 to 400 magnifications, on polished surfaces of each glass composition, to evaluate their homogeneity. The surface morphology and homogeneity were confirmed by back scattered electron SEM images and EDX point analysis which is shown in Fig. 2. Preliminary investigations by TEM on selected glasses showed no evidence of metallic inclusions, phase separation, or other heterogeneities and selected area electron diffraction patterns confirmed their amorphous nature. A high-resolution electron microscopy image of the $La_{6.63}Pr_{6.38}Si_{10}O_{16.07}N_{15.63}$ (*c.f.* Table 1) is shown in Fig. 3.

3.2. Glass properties

Measured densities and calculated molar volumes and compactness for the glasses in La–Pr–Si–O–N system are given in Table 2. The variation of the density as a function of Pr content is shown in Fig. 4. The density, molar volume and compactness of only La containing glass (no. 1 in Table 2) is 5.12 g/cm^3, 9.13 cm^3/mol, and 0.567, respectively. The density varies between 5.12 and 5.49 g/cm^3 and increase with the substitution of Pr content for La. The molar volume (MV) value varies between 8.59 and 9.35 cm^3/mol (Table 2), it is difficult to see systematic variation in the MV but slightly decrease with the substitution by Pr for La. The glass compactness values vary between 0.558 and 0.596 and increase by the substitution of Pr for La.

Observed glass transition temperatures, T_g, and crystallization temperatures, T_c for glasses with different amounts of modifiers are listed in Table 2. The glass transition temperatures range from 1050 to 1090 °C, and crystallization temperatures from 1200 to 1230 °C. Fig. 5 shows that there is a significant increase in T_g and T_c with the substitution of Pr for La. For La–Pr–Si–O–N glasses with constant Si:O:N ratios, the

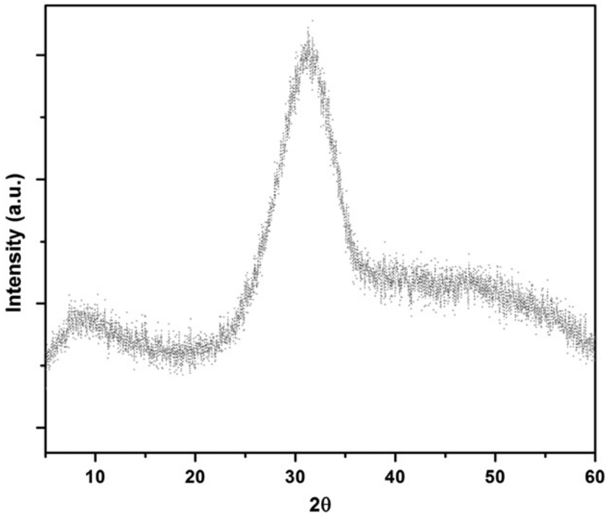

Fig. 1. XRD curve of glass 8 (*c.f.* Table 1).