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# Glass-to-crystal transition in the NASICON glass-ceramic system $Na_{1+x}Al_xM_{2-x}(PO_4)_3$ (M=Ge, Ti)

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ABSTRACT

The glass-to-crystal transition of $Na_{1+x}Al_xGe_{2-x}(PO_4)_3$ (NAGP), and $Na_{1+x}Al_xTi_{2-x}(PO_4)_3$ (NATP), both crystallizing in variants of the Na-superionic conducting (NASICON) structure, has been investigated by solid-state NMR. The ceramic materials produced by annealing the precursor glasses above the glass transition temperature are candidate materials for solid-state separator membranes in sodium ion batteries. The different local structural environments involving both network former and network modifier species have been characterized by comprehensive $^{23}Na$, $^{27}Al$ and $^{31}P$ magic angle spinning nuclear magnetic resonance (MAS NMR) experiments. In crystalline $Na_{1+x}Al_xGe_{2-x}(PO_4)_3$ samples multiple phosphate environments are observed, corresponding to *n* Al and 4-*n* Ge species in their second coordination spheres. In contrast, no site resolution is observed in the analogous $Na_{1+x}Al_xTi_{2-x}(PO_4)_3$ (NATP) system. This can be understood on the basis of X-ray powder diffraction (XRD) data, which reveal a significant lattice expansion in the former, but no lattice expansion in the latter material. $^{27}Al$ MAS-NMR data reveal that in the glassy state, Al occurs with coordination numbers four, five and six, with the fraction of four-coordinated Al being substantially higher in the NATP glasses than in the NAGP glasses. $^{23}Na$ MAS-NMR and spin echo decay measurements reveal distinct differences between glassy and crystallized materials with regard to the local environments and the spatial distributions of the sodium ions.

## 1. Introduction

Much effort in recent materials science has been focused on the development of energy storage devices which simultaneously possess high-energy and high-power properties [1,2]. From the viewpoint of cycling stability and operating safety all-solid-state batteries featuring fast-ion conducting electrolytes are preferred over batteries with liquid electrolytes [3–5]. The principal challenge lies with the creation of materials with sufficiently high ionic conductivity and general stability at atmospheric- and electrochemical conditions. Promising crystalline materials include solid electrolytes crystallizing in the Na-superionic conductor (NASICON) structure [6]. This versatile structure, featured by the general compositional formula: $A(I)_{1+2w+x-y+z}M(II)_wM(III)_xM(V)_yM(IV)_{2-w-x-y}(SiO_4)_z(PO_4)_{3-z}$ gives rise to a large family of highly conducting solid electrolytes. Here we consider crystalline solid solutions based on a fundamental composition $A(I)M(IV)_2(PO_4)_3$ in which the tetravalent ion M(IV) is substituted by trivalent ions. Charge balance is restored by incorporation of a corresponding amount of monovalent A cations (usually Li, Na or Ag), which are accommodated on interstitial sites in the structure [6,8]. Homogeneity regions depend on cation radius ratios and also turn out to be strongly influenced by preparation and processing conditions. While materials have been traditionally prepared via solid-state reactions ("sintering route"), preparations involving the crystallization of precursor glasses ("glass-ceramic route") have resulted in more homogeneous materials with controllable microstructures and morphologies [7]. The NASICON structure features two distinct sites for the monovalent species, called A1 and A2, which are present in a ratio of 1:3. The preferred ionic pathway is assumed to involve a sequence of A1→A2→A1 jumps through interstitial windows [9]. As the latter present the kinetic bottleneck of ionic motion, recent studies have attempted to modify window sizes, by substituting the M(IV) ion either isovalently or aliovalently by a trivalent ion such as $Al^{3+}$ or $Cr^{3+}$ [10–18].

While the majority of work on NASICON publications focuses on lithium-containing systems, the parallel exploration of sodium-bearing materials is motivated by the (compared to lithium) 500-fold atomic

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abundance of the element sodium in the earth's crust and its much more widespread geographical distribution. Thus, large-scale efforts will be sustainable and attractive to national energy economies. In the present contribution, we discuss glasses and glass-ceramics of composition $Na_{1+x}Al_xGe_{2-x}(PO_4)_3$ (NAGP) and $Na_{1+x}Al_xTi_{2-x}(PO_4)_3$ (NATP) ($0.4 \le x \le 1.0$) together with NGP, the aluminum free composition ($x = 0$). This study extends previous works reporting electrical conductivities and standard solid state characterization of exclusively crystalline members of the NAGP [19,20] and NATP [21] families in the compositional regimes of $0.3 \le x \le 1.0$ and $0 \le x \le 0.9$ respectively, and allows a comparison with respect to the related lithium NASICON materials [11,22]. In particular, we will make extensive use of solid-state nuclear magnetic resonance (NMR) spectroscopy, to characterize the glass-to-crystal transition in the NAGP and NATP systems. While NMR has already been widely applied for the study of lithium-containing NASICON materials [11,23–29] results on crystalline sodium-containing NASICON powders are scarce [30,31] and to date, no experimental characterization of the precursor glasses and of glass-ceramic materials has been done.

## 2. Experimental section

### 2.1. Sample preparation and characterization

Vitreous $Na_{1+x}Al_xM_{2-x}(PO_4)_3$ (M = Ge, Ti) samples were prepared in 20 g batches by the standard melt-quench process and subsequent heat treatment. Finely ground $Na_2CO_3$ (Vetec, 99.5%), $Al_2O_3$ (Aldrich 99%) $GeO_2$ (Aldrich 99%), $TiO_2$ (Aldrich 99.9%) and $NH_4H_2PO_4$ (Aldrich 98%) were mixed in the ratios corresponding to the desired sample compositions (listed in Table 1) and heated in a platinum crucible in three steps: (1) heating from room temperature to 673 K at 10 K/min with a holding time of 4 h at 673 K (2) heating to 973 K at 10 K/min, and holding time of 2 h at 973 K to ensure the complete removal of $CO_2$, $NH_3$ and $H_2O$, (3) melting for 30 min at 1573–1653 K, and 1723 K for NAGP and NATP glass respectively. To ensure homogenization, glasses were splat-cooled after 30 min, then remelted at same temperature for more 30 min. After rapid splat cooling, small brittle glass pieces of 1.5 mm thickness and areas ranging from 10 to 100 $mm^2$ were obtained. NAGP glasses were transparent and colorless, while NATP glasses were violet-colored and contained, depending on the aluminum content, spots of crystalline phase, reflecting the great tendency of these glasses to crystallize. This purple color was already found in the lithium homologue, LATP glass and was attributed to the presence of $Ti^{3+}$ ions, reduced from $Ti^{4+}$ during the melting procedure [12]. Glass transition ($T_g$) and crystallization temperatures ($T_x$) were measured by differential scanning calorimetry (DSC) on a DSC 404 NETZSCH system (heating rate 10 K/min).

Glass-ceramics were obtained by a heat treatment of the precursor glasses at each composition's crystallization temperature (temperature $T_x$, measured at the onset of the crystallization peak), for 3 h and 30 min, for NAGP and NATP. $T_x$ varied with the increase in Al content, from 919 to 939 K for NAGP and from 940 to 992 K for NATP. In the case of crystallization heat treatment, samples were inserted directly in a pre-heated oven at $T_x$ to avoid nucleation upon heating. The crystalline phases of the glass-ceramics were characterized by X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer, operating with Cu $K_\alpha$ radiation generated at 20 mA and 40 kV and integration times of 0.6 s at 0.02° steps. Diffraction peak indexing and lattice constant analysis was done using the QualX [32] and Expo2014 [33] software by Altomare et al., in combination with the Crystallography Open Database (COD) [34]. Densities were obtained by Archimedes' principle using an analytical balance and water as fluid media.

### 2.2. Solid state NMR

NMR spectra were obtained at 11.7 T (Bruker DSX-500), 9.4 T (Bruker DSX-400), 5.7 T (Varian 240-MR DD2) and 4.7 T (Bruker DSX-500 console) with commercially available 4 mm triple resonance MAS probes and MAS spinning rates varying from 10.0 to 15.0 kHz. The data were analyzed with the DMFIT software package [35]. $^{31}P$ MAS NMR spectra were measured at 98.12 MHz with $\pi/2$-pulse durations of 4 µs length and recycle delays of 1200 to 1400 s. Chemical shifts are reported relative to $-85\%$ $H_3PO_4$, using $BPO_4$ at -29.3 ppm as a secondary standard. The spectra were deconvoluted into Gaussian components. $^{27}Al$ MAS NMR spectra were measured at 63.16 MHz using pulses with small flip angles (30°) of 1.3 µs duration and recycle delays of 0.5 to 1 s. Chemical shifts are reported relative to 1 M aqueous solution of $Al(NO_3)_3$ using solid $AlF_3$ as a secondary standard.

$^{23}Na$ MAS NMR spectra were measured at 64.12 MHz using small flip angle pulses (30°) of 0.7 µs duration and recycle delays varying between 0.25 and 5 s. The chemical shifts are reported using solid NaCl (7.2 ppm vs 1 M aqueous NaCl solution [36]) as a secondary reference. The central transition spectra of these quadrupolar nuclei were fitted according to the Czjzek model [37]. $^{23}Na$ Triple Quantum Magic Angle Spinning (TQMAS) spectra were recorded at carrier frequencies of the standard MAS NMR experiments using a three-pulse sequence with z-filter [38]. The employed pulse lengths were close to 4.8 and 1.8 µs at a nutation frequency of 114 kHz for the first two hard pulses. The duration of the soft third pulse was 9.5 to 11.0 µs at a nutation frequency of 12.5 kHz. All the samples were spun at the magic angle with a frequency of 14.0 kHz. Acquisition of the indirect dimension was synchronized with the rotors' spinning speed and for sampling in the $t_1$ dimension dwell times of 18 to 36 µs were chosen. The data is shown after shearing transformation with sum projections of the high and low-resolution spectra along the $F1$ and $F2$ axis respectively. In order to obtain values of the second order quadrupole effect (*SOQE*) and the isotropic chemical shift ($\delta_{CS}^{iso}$) the signal's center of gravity in $F1$ and $F2$ dimension was evaluated. Homonuclear $^{23}Na-^{23}Na$ dipole-dipole coupling strengths were determined by the static Hahn spin echo decay method [39,40]. Selective excitation of the central $m = 1/2 \leftrightarrow m = -1/2$ Zeeman transition was achieved using a $^{23}Na$ nutation frequency of 10.4 kHz for non-selective excitation, corresponding to $\pi$-pulse durations of about 24 µs for the solid samples. The homonuclear dipolar second moments $M_{2(Na-Na)}$ were determined from the Gaussian decay $I(2t_1)/I(0) = \exp(-2M_2t_1^2)$ at short evolution times ($2t_1 < 500$ µs). The experimental values were compared with those calculated from the closest Na–Na distances within the data range 0–30 Å [41,42] in the crystal structures of NTP and NGP.

$^{31}P-^{27}Al$ dipole-dipole interactions were measured using $^{27}Al\{^{31}P\}$ rotational echo double resonance (REDOR) and $^{31}P\{^{27}Al\}$ rotational echo adiabatic passage double resonance (REAPDOR) experiments [43]. The $^{31}P$ $\pi$-pulse length of 5.0 µs was adjusted by maximizing the difference signal $\Delta S$ at a fixed dephasing time and the $^{27}Al$ $\pi$-pulse length was 6.1 µs. Further, REAPDOR NMR experiments were performed at a rotor speed of 12.0 kHz, with a $^{31}P$ $\pi/2$ pulse length of 3.1 µs and a $^{27}Al$ adiabatic pulse duration of 27.8 µs. High resolution $^{27}Al$ and $^{31}P$ MAS NMR spectra were extracted and shown to allow a comparison of signal amplitudes without ($S_0$) and with ($S$) $^{31}P$ pulse irradiation after a dipolar mixing time of 16 rotor cycles.

## 3. Results and discussion

### 3.1. Macroscopic properties

Fig. 1 shows the DSC curves of the two series of glass samples investigated and the obtained glass transition temperatures are summarized in Table 1. The NATP glasses are distinguished by substantially higher $T_g$ values compared to the NAGP glasses. In both series $T_g$ and $T_x$ tend to decrease with increasing Al content. Densities of glass ceramics are close to those measured in the glass state (up to only 5% higher) and decrease with increasing x value in both systems. Glassy NTP ($x = 0$) could not be obtained even by rapid quenching of the melt. The XRD