

Sodium ion transport in polymorphic scandium NASICON analog $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ with new dielectric spectroscopy approach for current-constriction effects

Su-Hyun Moon, Yoon Hwa Kim, Dong-Chun Cho, Eui-Chol Shin, Donghwa Lee, Won Bin Im, Jong-Sook Lee *

School of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea

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ABSTRACT

Conductivity, calorimetry, and in-situ XRD can be closely interrelated with each other in terms of the sodium ion ordering and rearrangements in NASICON structure. An intermediate phase transition at 103 °C, not associated with heat effects, is evidenced for the first time, in addition to α – β and β – γ phase transitions at 64 °C and 166 °C. AC characterization of polycrystalline $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ has been performed over the wide temperature range from 225 to –100 °C. Strongly dispersive spectra of the low temperature monoclinic phase were systematically described by the total sample resistance connected by the several capacitive responses all in parallel: pure dielectric geometric capacitance and two Havriliak–Negami (HN) dielectric functions with opposite skewnesses. The capacitance strengths of HN functions are inversely proportional to the temperature and the relaxation times represent the thermally activated mobile charge carrier transport. While the higher frequency response with a negative skewness as $\gamma = 0.388$ and $\beta = 1$ is of a universal character common with many other solid electrolytes, known as K1 model, the lower frequency response with a positive skewness as $\gamma \cdot \beta \approx 1$ where $\beta \approx 0.59$ and $\gamma \approx 1.67$ describes the current-constriction effects occurring in the polycrystalline $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$. The current-constriction effects are described by a homogeneous polarization throughout the sample with 4 times the hopping distance and 5 times the relaxation time of the K1 response. 14 model parameters competently simulate the AC behavior over a wide temperature and frequency range.

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1. Introduction

The dispersive response is universally observed in many solid electrolyte systems which is characterized by the power-law dependence of AC conductivity as $\sigma \propto \omega^\alpha$ with α specifically near 0.6 [1–10], although not yet sufficiently widely acknowledged in the concerned research community. That it scales together with DC conductivity indicates the mobile charge carrier origin. A constant phase element (CPE) model or Q model with $C_Q^* = Q(j\omega)^{\alpha-1}$ and $\alpha \approx 0.6$ in parallel to an almost ideal capacitance element for the true dipolar dielectric response, describes approximately the frequency dependence of complex variables. According to Macdonald [4–9,11] the dispersive frequency corresponds to the Laplace–Fourier transform of the stretched exponential temporal response, $\exp(-t^{\beta_k})$ with $\beta_k = 1/3$, which is named as K1 model. CK1 model emphasizes the presence of a frequency-independent dielectric capacitance, which is not considered in the conductivity spectroscopy. The exact frequency response is given by the free LEVM CNLS fitting program with open Fortran sources [9]. It is associated with a polarization strength proportional to the mobile charge carrier concentration and the time constants for the conduction process. These aspects

cannot be properly described by a CPE. For the sake of convenience in a layman's analysis an approximate closed-form expression of K1 model has been recently suggested as a Cole–Davidson type dielectric function [12]

$$C_{CD}^* = \frac{C_{CD}}{(1 + i\omega\tau_{CD})^\gamma} \quad (1)$$

with $\gamma = 0.388$ in describing the dispersive bulk response in the β'' -alumina [13] and AgI [14]. The Cole–Davidson dielectric function can represent the strength of the polarization from the mobile charge carriers by C_{CD} and the intrinsic dc conduction mechanism by the temperature dependence of the time constants, τ_{CD} , as in the exact CK1 model [11].

The closed-form approximation of CK1 behavior allowed the authors to conveniently combine additional polarizations due to the grain boundaries and/or electrodes [13,14]. It is notable that the severely overlapping current-constriction effects in polycrystalline β'' -alumina were successfully described by additional Cole–Davidson dielectric functions which are connected parallel to the bulk dipolar dielectric capacitance and the Cole–Davidson dielectric function for the CK1 response [13]. A Cole–Davidson dielectric function with a thermally activated τ_{CD}^{-1} can represent

* Corresponding author.

E-mail address: jongsook@jnu.ac.kr (J.-S. Lee).

current-constriction or grain boundary resistance defined by the low-frequency limit of the real impedance (Z') [13].

It should be emphasized that the 'Q' elements widely employed as generalized capacitors do not provide well-defined capacitance magnitudes, which are often needed for the evaluation of material parameters. Often, an effective or an average capacitance C_{equiv} is estimated for the depressed semicircular impedance described by RQ as $\omega_p = (RQ)^{-1/\alpha} = (RC_{\text{equiv}})^{-1}$, from which bulk dielectric constants or space charge layer widths are derived, e.g. [15]. However, there is no rigorous theoretical basis for such an estimation. The power exponent α parameters vary arbitrarily to minimize the sum of the squares in the non-linear least squares fitting procedure and thus become strongly correlated with other fit parameters. Moreover, even with such a free adjustability, the RQ models do not satisfactorily describe dispersive experimental responses in the wide frequency range. Limited spectral ranges visible in the complex plane representations are often suggested to have been 'well-fitted'.

The inappropriateness of modeling with 'Q' elements can be immediately seen in the AC behavior of real solid electrolytes: Series of dispersive responses at different temperatures indicate rather well-distinguished capacitive effects [13,14]. The parallel network of the capacitance functions is then a plausible model, rather than the conventional series network of impedance functions. Hence, the new approach essentially follows the textbook dielectric spectroscopy where all the polarizations are added as shown in Fig. 1, e.g. [16]. The relaxation times of 'space charge polarization' at grain boundaries ϵ_{GB} [16] and ϵ_{C} , an additional contribution in the solid electrolyte systems described by K1 model, are shown similarly temperature-dependent. The response with a dielectric strength ϵ_{D} for a possible dipolar contribution may have a different, probably weaker, temperature dependence. For the frequency range generally concerned, the high frequency response can be modeled essentially temperature- and frequency-independent dielectric constant, ϵ_{S} comprising ionic and electronic (atomic) polarizations, ϵ_{ion} and ϵ_{e} . The dispersive behavior was represented by the well-defined, temperature-independent, exponent γ_{CD} in Cole–Davidson dielectric functions [13,14]. Since the parameters of the equivalent circuits based on the new approach are either constant or well-defined in the temperature dependence, the AC response can be simulated over a wide range in frequencies and temperatures using model parameters only around 10 in number [13,14].

Since the pioneering work in seventies and eighties [17–20] the NASICON or $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ system is probably the next famous sodium ionic conductor after beta alumina system. NASICON structure compounds with transition metals are also actively investigated for applications in battery electrodes [21,22]. Among phosphate solid solutions $\text{Na}_{1+x}\text{M}_x\text{Zr}_{2-x}(\text{Si}_y\text{P}_{1-y}\text{O}_4)_3$ (NZSP) where $\text{M} = \text{Al}, \text{Ga}, \text{Cr}, \text{Fe}, \text{Sc}, \text{In}, \text{Y}, \text{Yb}$ [23] $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ exhibits the closest structural similarity with true Zr NASICON and the highest room temperature sodium ion

conductivity. Since untwinned single crystals were available for the determination of the crystal structure, the ionic distribution, the ion-ion correlation and the conduction mechanism, the system was actively studied in the Eighties [24–32]. Publications after decades of dormancy can be found [33–35].

Similarly as in Cr, Fe, or V NASICON analogs [22,36–39], the scandium NASICON analog exhibits a transition to the 'superionic' rhombohedral state (γ) with a very low activation energy around 166 °C. The monoclinic (α)–rhombohedral (β) phase transition at 64 °C involves a step-wise change in conductivity. Somewhat different structural transitions were reported for differently prepared single crystalline samples [31–34,38] and also in polycrystalline samples [30,35]. In early work on NASICON materials conductivity was monitored at a fixed frequency, e.g. 500 kHz [17] or $\omega = 10^4 \text{ s}^{-1}$ (1.6 kHz) [40], which was supposed to give the sample conductivity unaffected by the electrode polarization. However, the strong frequency dispersion due to the grain boundaries were noted [41,42]. The difficulty in application of Bauerle's model or brick-layer model for the grain boundary effects in NASICON materials was discussed [42,43]. For scandium analog, overall sample conductivity was estimated with accuracy in apparently varying degrees [24–26, 29–32]. The grain boundary effects have not been properly addressed.

In this work the AC behavior of a polycrystalline $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ is thoroughly examined. The overall sample conductivity above room temperature is compared with the phase transitions between α , β , and γ indicated by the differential scanning calorimetry and in-situ XRD. A notable correlation between the conductivity and the peak intensity variation is found. While the overall sample response is well distinguished from the electrode polarization, the low temperature monoclinic (α) phase indicates the current-constriction grain boundary impedance strongly overlapped with a high frequency bulk impedance of a similar magnitude. As shown for polycrystalline beta alumina [13], instead of the conventional brick-layer modeling, parallel connected capacitance functions to the overall sample resistance are shown to competently describe the overall AC response. The approach is further developed for a NASICON material and physical interpretations are provided. It is suggested that Havriliak–Negami dielectric functions can be applied to the current-constriction effects in polycrystalline electrolytes, generalized from the Cole–Davidson type employed in the earlier work for β' -alumina [13].

2. Experimental

$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ samples were prepared by solid state reaction method using raw powders of Na_3PO_4 (Aldrich, 96.0%), Sc_2O_3 (Kojundo, 99.9%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Junsei, 99.0%). The mixture was fired at 350 °C for 1 h in air to decompose $\text{NH}_4\text{H}_2\text{PO}_4$, ground again, cold isostatically pressed, and fired at 1300 °C for 3 h in 25% H_2 /75% N_2 covered by the powdered mixture to avoid sodium loss. The sintered density of the samples was measured by the Archimedes method, where the surface of the porous

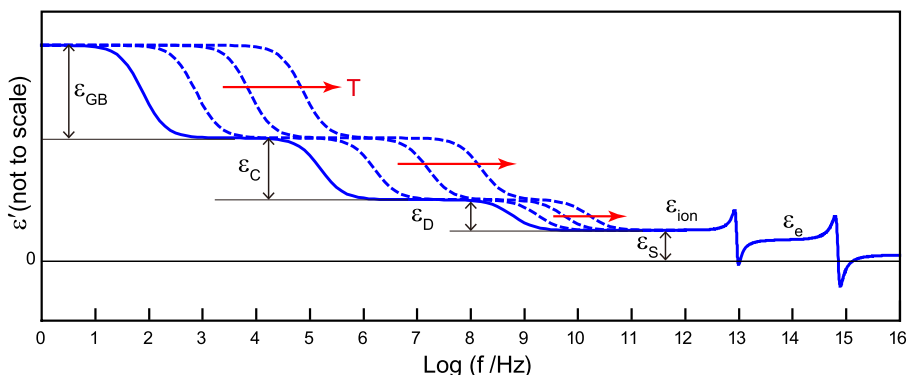


Fig. 1. Variation of the dielectric constants with frequency for a polycrystalline ceramic ionic conductor.

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