Structure, Ionic Conduction and Dielectric Relaxation in a Novel Fast Ion Conductor, $Na_2Cd(SO_4)_2$

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Solid electrolytes (fast ion conductors) are a class of materials that exhibits high ionic conductivity at relatively (approximately 10^{-3} to 10^{-1} S/cm) modest (500−700 °C) temperatures. In recent times, microporous materials have been used to mobilize extra framework cations and thus induce high ionic conductivity.[1] Extensive research on crystalline solid electrolytes like, for example, Nasicon and Lisicon,[2−4] Bimivox,[5,6] and rock salts[7] has resulted in generating several potential ionic conductors. The ions that normally conduct are Li^+, Na^+, H^+, K^+, Ag^+, O^{2-}, and F^-. Room temperature conductivity of 0.3 S/cm has been observed in Ag and Cu halide systems.[8,9] Further binary lithium halide systems (for example, LiI−RbI[10]) have been investigated for high ionic conductivity. We have been interested in bimetallic sulfates as possible ionic conducting materials, and a novel structural type represented by the compound $Na_2Cd(SO_4)_2$ has been synthesized and characterized by single-crystal X-ray diffraction. Furthermore, the compound displays high ionic conductivity (6.1×10^{-2} S/cm at 600 °C). In this communication, we report the features of this structure, the ionic conductivity behavior with temperature, and its correlation with dielectric relaxation and differential thermal analysis.

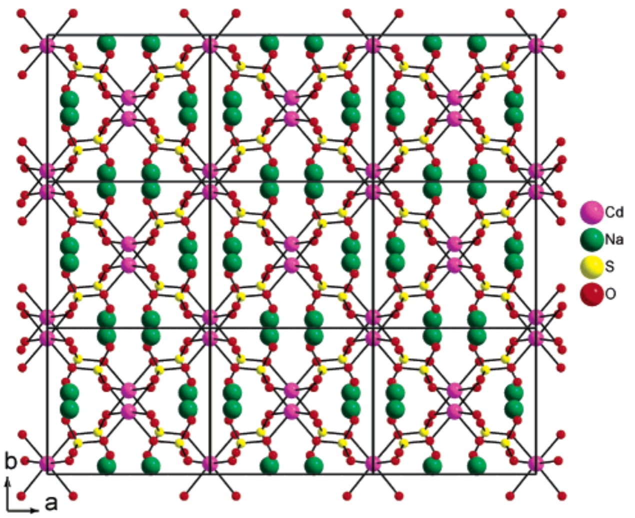

Figure 1. Packing diagram of $Na_2Cd(SO_4)_2$ viewed down *z*-axis.

Table 1. Bond Lengths and Bond Valence Sums in $Na_2Cd(SO_4)_2$

measure	distance	BVS	measure	distance	BVS
Cd1−O2	2.238(2)	0.344	Na1−O4	2.322(2)	0.246
Cd1−O2′	2.238(2)	0.344	Na1−O3	2.363(2)	0.220
Cd1−O4	2.330(2)	0.316	Na1−O3′	2.405(2)	0.197
Cd1−O4′	2.330(2)	0.316	Na1−O1	2.560(3)	0.129
Cd1−O1	2.382(2)	0.257	Na1−O3″	2.623(2)	0.109
Cd1−O1′	2.382(2)	0.257	Na1−O4	2.652(2)	0.101
	sum =	1.834	Na1−O2	2.882(3)	0.054
S1−O1	1.458(2)	1.566	Na1−O2′	3.009(3)	0.038
S1−O2	1.468(2)	1.524		sum =	1.094
S1−O3	1.468(2)	1.524			
S1−O4	1.478(2)	1.484			
	sum =	6.098			

Single crystals of the compound were grown by slow evaporation from an aqueous solution containing equimolar quantities of Cd_2SO_4 and Na_2SO_4. X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer. The X-ray generator was operated at 50 kV and 40 mA using Mo Kα radiation. For all the measurements, 606 frames per set were collected using SMART[11] in four different settings of φ (0°, 90°, 180°, 270°) with the ω-scan at −0.3° intervals with a counting time of 15 s, keeping the sample to detector distance 6.062 cm and the 2θ value fixed at −28°. The data were reduced by SAINTPLUS,[11] an empirical absorption correction was applied using the package SADABS,[12] and XPREP[11] was used to determine the space group. The structures were solved and refined using the SHELXL-97[13] program available in the WinGX[14] suite. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional R-factors R are based on F.[15] Ionic conductivity was measured on a sintered pellet by using a HP194A impedance/Gain phase analyzer over the frequency range 100 Hz−15 MHz in the temperature range 100−600 °C in air. The sample was equilibrated at constant temperature for about 30 min prior to each impedance measurement, and the conductivity was obtained from the low frequency intercept of the impedance plot. Differntial thermal analysis (DTA) measurements were done on a TA Instruments SDTQ600. The ramp rate was fixed at 5 °C/min in air

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(15) Crystal data: chemical formula $Na_2Cd(SO_4)_2$; formula weight = 350.53; monoclinic, space group *C*2/*c*; $a = 10.059(2)$ Å, $b = 8.2250(18)$ Å, $c = 8.6557(19)$ Å; $\beta = 114.620(2)$°; $V = 651.0(2)$ Å^3; $Z = 4$; $\rho_{calc} = 3.576$ g/cm^3; $T = 293$ K; $\mu = 4.134$; refelction measured = 3549; unique reflection = 799; observed $[I > 2\sigma(I)] = 791$; $R[F^2 > 2\sigma(F^2)] = 0.018$; $wR(F^2) = 0.047$.

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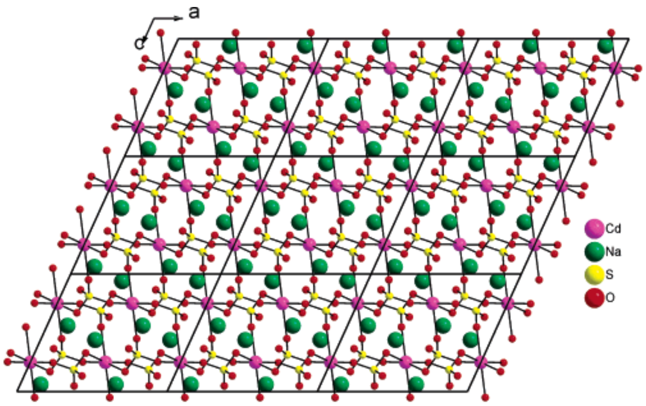

Figure 2. Packing diagram of $Na_2Cd(SO_4)_2$ viewed down *y*-axis.

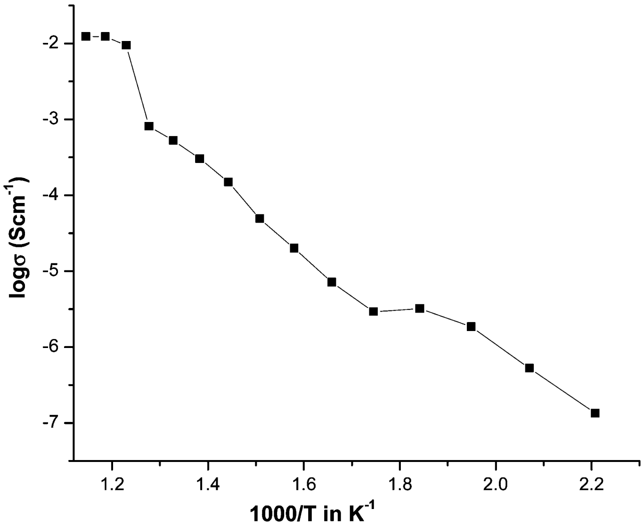

Figure 3. Temperature-dependent conductivity of $Na_2Cd(SO_4)_2$.

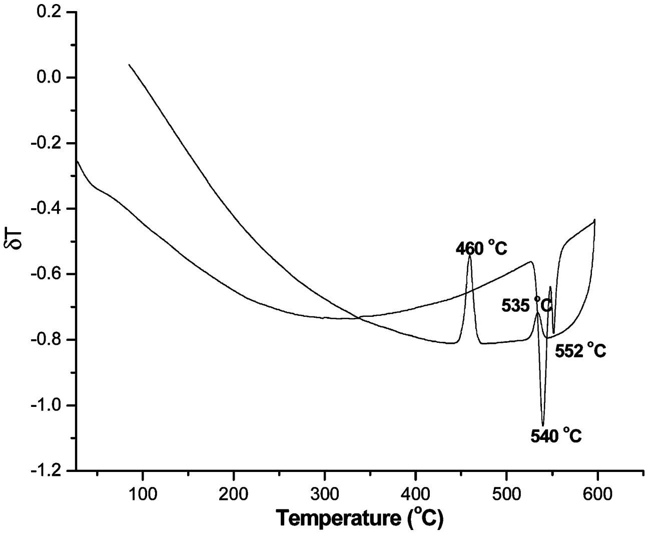

Figure 4. DTA curve of $Na_2Cd(SO_4)_2$.

atmosphere. The capacitance and dielectric loss (*D*) were measured as a function of both frequency (100 Hz−10 MHz) and temperature (25−400 °C), at a signal strength of 0.5 V_{rms} using impedance gain analyzer (HP4149A). An in-house built high-temperature cell was used during this measurement.

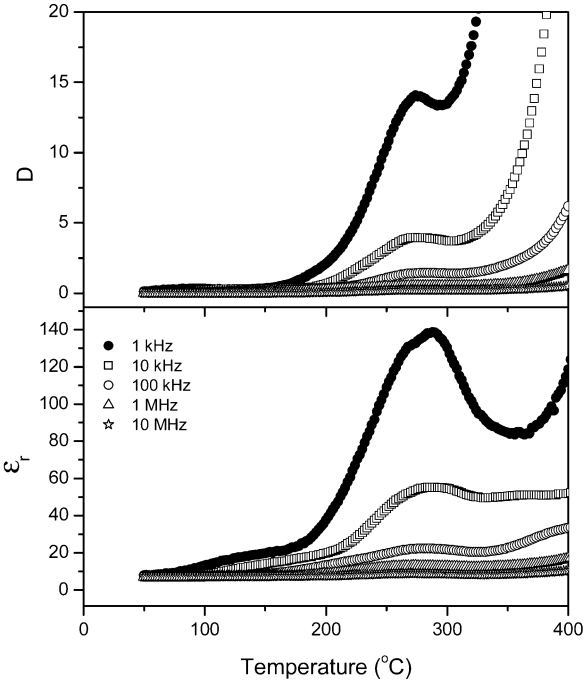

Figure 5. Temperature dependence of the dielectric constant as function of frequency of $Na_2Cd(SO_4)_2$.

The crystals belong to the space group *C*2/*c*, and details of the crystal data collected on a Bruker CCD APEX system give 799 independent reflections refining to a final *R*-factor of 0.018.[15] Figure 1 shows the packing diagram as viewed down the *z*-axis. The structure is built of alternating sulfate tetrahedra linking to Cd octahedra forming a chain along the [110] direction which in turn is cross linked with a chain running 90° to this plane effectively generating a two-dimensional framework. The Cd atom has two short, two medium, and two long bonds with symmetry-related oxygen atoms, as can be seen from Table 1. Likewise the S atom has one short, two normal, and one long tetrahedral bond while the Na atom located in the two-dimensional framework is generating a weak eight-coordinated link extending along the *z*-axis forming a channel-like structural motif (Figure 1). Indeed, the Na atoms are located in the space generated by the combination of covalently bound octahedra and tetrahedra as shown in Figure 2. This suggests the possibility of facile Na^+ ion migartion through the framework, and the rather high ionic conductivity of 10^{-2} S/cm at 600 °C appears as a consequence. The bond valence sums (Table 1) confirm the assignments of the cationic sites.

It is of interest to note that a dihydrate of the same material $[Na_2Cd(SO_4)_2{\cdot}(H_2O)_2]$ was reported earlier[16] to belong to a monoclinic kröhnkite structure [space group $P2_1/c$]. This structure forms infinite chains, composed of $CdO_4(H_2O)_2$ octahedra alternating with each two SO_4 tetrahedra by sharing corners. Na−O bonds and hydrogen bonds link the chains to layers and further onto the three-dimensional structure. Thus, the structure of $Na_2Cd(SO_4)_2$ is novel and generates the required channels for Na^+ ion migration.

The features associated with the conductivity behavior show two possible transitions, one at ~280 °C and the other at ~552 °C (Figure 3). The value of the conductivity is 4.6 × 10^{-5} S/cm at 280 °C, which increases to a value of 4.6 ×

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10^{-2} S/cm at 552 °C. This observation is substantiated by the DTA data (Figure 4), which shows transitions corresponding to the temperatures shown by the conductivity behavior. Furthermore, the DTA analysis ahows an intersting reversible bahavior, the transition on the heating cycle is observed at 540 °C followed by yet another one at 552 °C. On the cooling cycle, the transitions are observed at 535 and 460 °C showing a hysterisis behavior strongly indicative of the Na^+ ion conduction in the compound. In addition, dielectric measurements performed on the same pellet used for conductivity measurements provide supporting evidence of the transition observed at 280 °C (Figure 5). The frequency dependence of the dielectric constant shows no significant anamolies and decreases with increase of frequqncy from 100 Hz to 10 MHz.

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Supporting Information Available: CIF file for $Na_2Cd(SO)_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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