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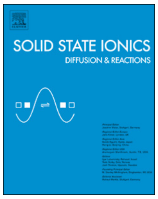

The effect of oxide additives on the transport properties of cesium nitrite

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ABSTRACT

Conductivity of composite solid electrolytes (1 − x) $CsNO_2$–xA (A = MgO, Al_2O_3, SnO_2) was systematically investigated. It was found that in all cases heterogeneous doping leads to the increase in the conductivity. Conductivity goes through a maximum as a function of the oxide concentration that is explained by additional contribution of the interface regions. However, in contrast to known composites, at small concentration of oxides the character of the Arrhenius dependences is similar to that of pure cesium nitrite, where intrinsic and extrinsic conductivity regions are observed. At high concentration of the heterogeneous dopant the character of Arrhenius dependences changes and no change in slope of the Arrhenius dependences is observed. According to thermal analysis data, at high concentration of oxide amorphous interface-stabilized phase of $CsNO_2$ forms on the oxide interface. Composite solid electrolytes based on $CsNO_2$ with additives of nanocrystalline γ-alumina and SnO_2 have a high ionic conductivities exceeding 10^{-2} S/cm at 356 °C. Composites containing additives of MgO have lower conductivity despite of high specific surface area.

1. Introduction

Search for new solid electrolytes with high alkali ion conductivity is a topical problem in solid state ionics. Plastic phases of ionic salts comprise a class of ionic conductors where high mobility of structural units, molecular groups of framework ions, facilitates transport of ions through the crystal lattice. In a series of alkali nitrites, nitrites of Na, K, Rb and Cs have orientationally disordered high-temperature phases. In particular, the high-temperature phase of $CsNO_2$ has a CsCl-type structure at the room temperature in which NO_2^- ions are statistically orientated over several directions in the crystal lattice. In literature there are data on structural, thermodynamic properties of cesium nitrite [1,2]. Cesium nitrite is known as a plastic crystal because it is mechanically soft, especially at high temperatures. The plastic CsCl-type phase, which called in the literature as $CsNO_2$-I, exists in the temperature range from 209.2 to the melting point of 673 K [3].

According to NMR data, there are two types of nitrite ion reorientation motions in phase I [4–6]. Reorientation mobility of anions should favor ionic transport. As it was shown [7–9], cesium nitrite has the highest conductivity in a series of alkali nitrites that is rather surprising due to largest ionic size of Cs^+ cations. The conductivity of $CsNO_2$ is relatively high and ranges from $5 \cdot 10^{-8}$ S/cm at 25 °C to 10^{-3} S/cm at 350 °C. Moreover, it has been shown that conductivity of $CsNO_2$ is ionic and the most probable type mechanism of the ionic transport was the migration of cationic vacancies [7–9]. In this regard, it would be possible to increase ionic conductivity owing to doping of $CsNO_2$ with nitrites of alkali-earth elements, e.g. $Ba(NO_2)_2$. Indeed, the introduction of Ba^{2+} cations into the crystal lattice of $CsNO_2$ leads to conductivity increase [9]; however, due to low solubility this effect is not high.

It is well known that heterogeneous doping may lead to a strong increase in the conductivity of ionic salts and may be used for search for or development of new solid electrolytes [10–18]. In earlier investigations it was demonstrated that addition of nanocrystalline oxides results in strong enhancement of conductivity of alkali nitrates [16,17], $LiClO_4$ [18]. Preliminary data on conductivity enhancement in alkali nitrites have been obtained also for alkali nitrites [8], however systematic studies of these composites over a whole series of alkali nitrites are in progress.

In this work we present the results of comparative study of physical properties and ionic conductivity of pure cesium nitrite and composite solid electrolytes based on $CsNO_2$ with additives of nanocrystalline oxides SnO_2, Al_2O_3 and MgO.

2. Experimental

Cesium nitrite was synthesized by the exchange reaction between water solutions of Cs_2SO_4 (99.9% pure, manufactured by Rare Metals

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Compounds Plant Co., Novosibirsk) and $Ba(NO_2)_2$ (Reakhim Co., 99.99%) taken in equimolar ratios followed by removal of $BaSO_4$ precipitate, evaporation of the solution and double recrystallization of the deposit. According to ICP-MS data (obtained on the Agilent 7500A Inductively Coupled Plasma Mass Spectrometer), cesium nitrite obtained by this technique contained concentration of impurities of Ba^{2+} cations of not > 20 ppm. Nanocrystalline oxides SnO_2 and MgO were prepared as reported earlier [19] and characterized by high specific surface area values, S_s, of 90 and 200 m^2/g for SnO_2 and MgO, respectively. Aluminum oxide, γ-Al_2O_3 (S_s = 200 m^2/g; specification, IKT-02-6M; manufactured by Catalyst Inc., Novosibirsk). The oxide powders were heated for 2 h at temperature of 600, 250 and 450 °C for Al_2O_3, SnO_2 and MgO, respectively, for removal of adsorbed water and surface hydroxyl groups. Brunauer–Emmet–Teller (BET) specific surface areas (S_s) were obtained with an automatic system ("Thermosorb TPD 1200", Katakon, Russia), using nitrogen gas. Prior to the analysis, the oxides were treated at 200 ° C for 1 hour. Composites $(1 - x)CsNO_2$-xA (A = SnO_2, Al_2O_3, MgO, x is the molar ratio, $0 < x < 1$) were prepared from preliminary dried components. Initial powders were mixed, heated at 390 °C for 30 min, cooled and compacted at 400 MPa together with two silver electrodes into pellets 0.1–0.2 cm in thickness and 0.5–0.6 cm in diameter. The values of density of the obtained tablets were 95–98% of the theoretical ones. The crystalline structure of the obtained composites was analyzed using X-ray diffraction technique. XRD patterns were recorded by a D8 Advance powder diffractometer with Θ-Θ geometry equipped with a one-dimensional Lynx-Eye detector and Kb-filter using Cu-Kα radiation in the interval of $5^\circ < 2\Theta < 90^\circ$ with a step size of $\Delta 2\Theta = 0.0195^\circ$ and a counting time of 35.4 s per step. The XRD structure analysis was performed by the Rietveld method [20] using Topas 4.2 software (Bruker AXS, Germany). The instrumental contribution was calculated using the method of fundamental parameters [21]. The initial structure information was taken from the Inorganic Crystal Structure Database (FIZ Karlsruhe, Germany). Differential thermal analysis (DTA) of samples (typical mass of the sample was 2-7 mg) was carried out at using 550 SSI Differential Scanning Calorimeter, the temperature variation rate was 10 K/min in the argon atmosphere. Conductivity was measured in a two-electrode cell in fore vacuum (2–4 Pa) in the temperature range 25–350 °C in stepwise isotherm mode with a Hewlett Packard HP 4284A Precision LCR Meter in ac-frequency range 20 Hz–1 MHz. The values of conductivity were calculated at each temperature by analysis of $Z'' = f(Z')$ impedance plots. Exposure time at each temperature before measurement was 10 min. At some separate temperatures the exposure time was 30 min to achieve complete equilibration of the sample. The data were well reproduced when measured on three subsequent heating-cooling cycles.

3. Results and discussion

3.1. Structural and thermal properties

On X-ray diffractograms of all composites under study one can see broadened reflections of nanocrystalline oxides and narrow peaks attributed to cesium nitrites. No peaks of other phases were observed suggesting that no chemical interaction between the phases took place during the synthesis. It is clearly seen from diffraction patterns for $CsNO_2$-SnO_2 composites shown in Fig. 1(a); qualitatively similar patterns were observed for also for composites $CsNO_2$-Al_2O_3 and $CsNO_2$-MgO. Rough estimation of the variation of the peaks intensities of $CsNO_2$ with the increase in the oxide content shows that (a) there is some redistribution of relative intensities between the different reflections indicating to structuring effects in composites (b) relative intensities of peaks decrease more strongly than could be expected for simple mixtures of the components. The last observation may be explained by partial amorphization of $CsNO_2$ which is more evident at high concentrations of oxides. This suggestion is confirmed by the refinement of X-ray diffraction patterns using a Rietveld analysis. Accordingly, at all concentrations of the oxide the calculated value of the weight fraction of the crystalline $CsNO_2$ in composites is considerably lower than the total quantity of the salt in the composite (Fig. 1(c)).

The formation of composites $(1 - x)CsNO_2$-xA (A = Al_2O_3, SnO_2) was investigated in situ by means of thermal analysis. The results of the study are presented in Fig. 1(b). Typically, on the first heating run the mixtures of $CsNO_2$ and the oxide additive heated up to temperature by 50° above the melting point of the salt. In all cases the peak corresponding to the melting enthalpy of $CsNO_2$ was observed. Then the sample was kept at high temperature for 20 min (for ionic salt could wet and spread along the surface of oxide) and slowly cooled down to room temperature. The DTA curve obtained on the second heating run corresponded to the composite prepared in situ in the DTA sample holder (aluminum pan). It should be noted that (a) at the $(1 - x)CsNO_2$-xA composites the melting temperature decreases with x by 2–10°; (b) at sufficiently high concentrations ($x > 0.5$ for Al_2O_3 and $x > 0.6$ for SnO_2) the heat effect attributed to the melting of the salt almost disappeared (see Fig. 1(b)). These effects may be caused by (a) decrease the effective particle size of salt in the composites and (b) formation of amorphous phase in the composites and almost complete transformation of $CsNO_2$ to an interface-stabilized amorphous state at high oxide concentrations. The latter effect was observed previously in systems $RbNO_3$-Al_2O_3 [22], $LiClO_4$-Al_2O_3 [18], $MeHSO_4$-SiO_2 (Me = Rb, Cs, K) [23,24]. Qualitatively, this result agrees with the data of X-ray Rietveld analysis. Nevertheless, according to X-ray data, complete amorphization of $CsNO_2$ occurs at x = 0.90 rather than x = 0.60. Possibly, weak heat effects cannot be resolved using standard DTA technique and for correct estimation of the concentration of the amorphous phase more accurate experimental techniques should be applied (Fig. 1(c)).

3.2. Transport properties

Fig. 2 shows impedance spectra recorded for composites $0.2CsNO_2$ - $0.8Al_2O_3$ and $0.1CsNO_2$ - 0.9MgO exhibited the highest conductivities. Similar impedance plots were also obtained for $CsNO_2$-SnO_2 composites. At low temperatures Nyquist plots represent as a single semicircle. As temperature increases, additional contribution of the electrode impedance appears in the low-frequency range which dominates at high temperatures. Such impedance spectra are typical for ionic conductors and may be satisfactorily described by simplified equivalent scheme which includes the bulk and electrode impedances connected in series (Fig. 2).

The bulk impedance includes two elements: the bulk resistance R_b and the constant phase element CPE_b; the electrode impedance comprises only the constant phase element CPE_e. The total conductivity values (σ) were calculated from the R_b values taking into account geometric parameters of the sample as $\sigma = (R_b \cdot S / d)^{-1}$, where, S is the electrode surface area and d is the pellet thickness. The conductivity values are well reproduced in the heating–cooling cycles and are stable under prolonged conditioning in vacuum under isothermal conditions.

As it has been shown by us earlier [8,9], conductivity of pure $CsNO_2$ obeys Arrhenius dependence log (σ) = f (1/T) with two regions with different slopes. Such behavior of conductivity is typical for classical ionic crystals and can be explained by the presence of temperature regions of intrinsic and extrinsic conductivity. The most appropriate data were obtained when the effect of the association of cation vacancies and impurity cations was accurately taken into account [8]. Calculated values of energy parameters of point defects determined from analysis of experimental data are $H_0 = 0.82$ eV and $H_m = 0.4$ eV for the Schottky defect formation energy and the migration energy for cationic vacancy, respectively [8].

Figs. 3–5 shows temperature and concentration dependences of conductivity for composites (1 − x) CsNO2-xA (A = SnO_2, Al_2O_3, MgO) under study.

One can note the following general trends in the conductivity